Noble Gases in Subduction Zones and Volatile Recycling

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INTRODUCTION

Volatiles are lost from the Earth's mantle to the atmosphere, hydrosphere and crust through a combination of subaerial and submarine volcanic and magmatic activity. These volatiles can be primordial in origin, trapped in the mantle since planetary accretion, or they may be recycled - re-injected into the mantle via material originally at the surface through the subduction process. Quantifying the absolute and relative contributions of these two volatile sources bears fundamental information on a number of issues in the Earth Sciences ranging from the evolution of the atmosphere and hydrosphere to the nature and scale of chemical heterogeneity in the Earth's mantle.

Noble gases have a pivotal role to play in addressing the volatile mass balance between the Earth's interior and exterior reservoirs. The primordial isotope ^{3}He provides an unambiguous measure of the juvenile volatile flux from the mantle (Craig et al., 1975). As such, it provides a means to calibrate other volatiles of geological and geochemical interest. A prime example is the CO_2 flux at mid-ocean ridges (MOR): by combining estimates of the ^{3}He flux at MOR with measurements of the $CO_2/^3$He ratio in oceanic basalts, Marty and Jambon (1987) derived an estimate of the CO_2 flux from the (upper) mantle.

This approach has also been extended to island arcs. Marty et al. (1989) found significantly higher $CO_2/^3$He ratios in arc-related geothermal fluids than observed previously (at MOR), consistent with addition of slab-derived CO_2 to the mantle wedge. Sano and Williams (1996) scaled the CO_2 flux to ^{3}He, showing that the output of CO_2 at subduction zones was comparable in magnitude to that at spreading ridges. Therefore, for CO_2 at least, subduction zones represent a major conduit for the loss of volatiles from the solid Earth. However, subduction zones are also the principal regions where materials (including volatiles) are returned to the mantle. For this reason, characterising volatile fluxes and inventories at subduction zones is crucial to understanding volatile budgets on the Earth and the nature of recycling between the mantle and the atmosphere, hydrosphere and crust.

In this contribution, we focus on the noble gas systematics of subduction zones. First, we review the various methodologies of sampling noble gases (and other volatiles) using fluids and rocks in both the subaerial and submarine environments. The aim is to give the reader background details on how the noble gas database was accumulated and some of the issues of concern regarding data integrity. We continue by cataloguing the noble gases systematics of both arcs and back-arcs (the output regions) – pointing out similarities and differences in the worldwide record. We highlight some of the major controversies in the interpretation of the database. Finally, we concentrate on the issue of volatile mass balance at subduction zones, emphasizing the role of the noble gases (especially ^{3}He) in constraining both the output fluxes of various volatile species and their provenance - both at individual arcs as well as on a global scale. We discuss implications of the volatile mass balance (or imbalance in some cases) for the recycling history of terrestrial volatiles between Earth's internal and external reservoirs.

SAMPLING FOR NOBLE GASES

Noble gases are found in all types of fluids and rock samples. For example, fumarolic gas discharges, bubbling hot springs, groundwaters, and natural gases are prime sampling media for noble gases, as are various minerals and submarine glasses which can be crushed or melted in vacuo to release their trapped volatiles. In this section, we review the principal means of sampling noble gases at subduction zones.

Volcanic and geothermal fluids

Volcanic and geothermal gas discharges are widely exploited for sampling magmatic volatiles. Various sampling techniques and strategies have been developed depending upon the circumstances of the gas discharge - particularly the temperature. In all cases, precautions are undertaken to avoid, or at least minimise, atmospheric contamination.

High temperature fumaroles on passively degassing volcanoes provide the opportunity to sample volatiles released directly from a magma body. Lower temperature gases associated with bubbling hot springs, usually located on the flanks of volcanoes, allow for the sampling of noble gases released via hydrothermal systems. To facilitate the transfer of high temperature (>400°C) gases into sampling containers, a silica glass tube (~1 inch diameter) is normally inserted into a gas vent. In the case of vents with discharge temperatures ranging from the boiling point of water to ~400°C, a titanium tube (~1 inch diameter) is used. Gases bubbling into hot springs are sampled by placing a plastic funnel under water - if possible, at the bottom of the spring. The silica/titanium tube or the funnel is connected via a glass connector and silicone or Tygon tubing to a sampling container, which is used for sample storage and transfer to the analytical facility. The following types of sampling containers are in common usage:

- Lead-glass flask (~50 cm^3 volume) with either one or two vacuum stopcocks. Lead-borate glass is used because of its low diffusivity for helium compared to Pyrex (helium diffuses 5 orders of magnitude slower through lead-borate glass than through Pyrex at 25°C; Norton, 1957). Bottles with two stopcocks (one on each end) allow for the flushing of the bottle with sample prior to collection. The inlet section of a single stopcock flask (previously evacuated to UHV) is usually configured in a "Y" shape to allow flushing of air from the connecting tubes prior to opening the valve and admitting the gas to the flask.
- The second type is the "Giggenbach" bottle used by most gas geochemists to obtain the total chemistry of gas discharges. The sampling bottle is an approximately 200 cm^3 evacuated glass flask (Pyrex or lead glass) equipped with a Teflon stopcock. The flask contains 50-80 cm^3 of 4-6N NaOH solution (Giggenbach and Goguel, 1989). The solution absorbs the reactive gases (CO_2, SO_2, H_2S, HCl, HF) allowing build up of a large partial pressure of the remaining (non-reactive) gases (N_2, H_2, O_2, CO, hydrocarbons and noble gases) in the headspace volume. An upside-down position of the bottle during storage, with the solution covering the Teflon stop-cock, helps prevent possible air contamination of the sample during long periods of storage. Gas splits for noble gas analyses are taken from the headspace of the sample bottle.

- The third sampling container consists of a copper tube (~10 cm^3) that is crimped using a cold-welder sealing device or pinched off using refrigeration clamps after collection of the sample (see Weiss, 1968; Kennedy et al., 1985). The clamps are designed to seal the tube by cold welding and are left in place until sample extraction. Copper is virtually impervious to helium, facilitating secure sample storage; however, interaction with high temperature, acid gases results in the formation of a mixture of copper sulphide, copper sulphate and copper chloride, which can impede the formation of a leak-tight cold seal (F.Goff, written communication, 2001).

During sample collection, it is critical to avoid air contamination. Usually this is not a problem at high flow-rate fumaroles as the sampling tube, silicone rubber tubing and sampling bottles are rapidly flushed with the discharging gas. At lower flow-rate fumaroles and bubbling hot springs, more care must be taken to effectively flush the sampling system. This is best achieved by leading a tube from the out-flowing side of the sample bottle into water, allowing the gas to flow through the sample system and bubble into water. Alternatively, a vacuum hand-pump may be used to facilitate flushing. Depending on the vigour of the gas discharges, flushing of the sampling system can take between ~5 and 40 minutes. Silicone tubes should be kept as short as practical in order to minimize the volume that needs to be flushed with gas prior to sample collection.

Gases from bubbling hot springs can also be sampled using the water-displacement method as described by Craig (1953), Mazor and Wasserburg (1965) and Kennedy et al. (1988). A funnel is submerged in the spring and the entire sampling apparatus is purged with spring fluids using a hand pump. The funnel is then inverted over the upwelling gas bubbles and the gas is allowed to displace all the water in the apparatus - with the exception of the copper-tube sampler, which is connected to the flow-through sampling line via a "Y" connection. After a steady flow of gas is attained through the sampling line, the liquid from the copper-tube sampler is displaced. This technique maximizes the volume ratio of the displacing gas to that of the displaced liquid and minimizes the effect of back solution of gas into cooler fluid as it is displaced. While filling the copper-tube with gas, the outside of the tube may be cooled with water (or snow/ice) in order to lower the vapour pressure of the water. Holding the tube vertical during sampling allows for the condensed phase to flow out and a steady flow of condensed liquid and non-condensable gas is maintained. This technique, therefore, facilitates collection of non-condensable gas at ambient pressure and cooler than ambient temperatures (see Kennedy et al., 1988).

Hot spring waters and groundwaters
Noble gases dissolved in groundwaters and hot spring waters can be sampled in a fashion similar to that of gas discharges from fumaroles. The most common sampling device is a copper tube, either cold welded or crimped shut using refrigeration clamps. A Tygon tube is connected to one end of the copper tube and inserted as deeply as possible into the mouth of the spring. A second Tygon tube is attached to the other end of the copper tube with the discharging water flowing through the tube assembly. After flushing the system

for a few minutes and tapping the copper tube lightly, e.g., with a wrench or screwdriver to release air bubbles from the walls of the copper tube, the tube is crimped shut. To avoid air contamination, the out-flowing end of the tube should be crimped first followed by the up-stream end.

Water samples can also be collected using evacuated flasks or "Giggenbach" bottles (without the caustic solution). As the spring water fills the evacuated bottles, dissolved gases will ex-solve and create a head-space in the bottle. Volatiles of interest, including the noble gases, can be withdrawn from the head-space volume for analysis.

Water samples from deep hot spring pools can be sampled at depth by use of a sampling device attached to an extension (aluminium) pole (Kennedy et al., 1988). This technique minimises air contamination due to entrainment of circulating air-saturated waters from the surface of the pool. A copper tube is fastened to the aluminum pole with a Tygon tube attached to the bottom end of the copper tube. A second Tygon tube is attached to the top end of the copper tube and to the pole, and left open to the atmosphere. A spring-loaded Nylon clamp is attached to the pole below the copper tube and triggered by a stainless steel cable that allows for the release of the clamp and the pinching of the Tygon tube. A second Nylon clamp is attached to the pole above the copper tube. For sample collection, the sampling device is kept vertical and lowered into the pool. At depth, the spring-loaded clamps are released, pinching the Tygon tubes. The device is brought back to the surface, maintaining the hydrostatic head of the sampling depth. At the surface, the copper tube is pinched shut using a cold welding device or refrigeration clamps.

Groundwater pumped from wells is normally sampled using copper tubes which are connected to the well by Tygon tubing. Caution must be exercised to sufficiently flush the sample device prior to crimping the copper tube. A "Y" connection may be used to release excess water pressure during and after pinching of the copper tube.

Geothermal wells
Gases from geothermal wells are collected in the same fashion as fumarole discharges. At geothermal wells, however, it is necessary to use a steam separator in order to efficiently sample the non-condensable gases, which partition into the steam phase. The collected sample then consists of steam plus gas.

Natural gases
Natural gases are generally CH_4-rich and at high pressure, making the sampling devices described above impractical. Natural gases are collected into 500 cm^3 or 1000 cm^3 "Whitey" stainless steel gas cylinders sealed at both ends with high-pressure valves. The pre-evacuated cylinders are either attached directly to the well-head or to the vapour-side of a gas-liquid separator. Once attached, the cylinders are opened, flushed with sample gas and sealed. In the laboratory, the cylinders are attached to a vacuum line and aliquots of the sample are transferred into copper tubes (Hiyagon and Kennedy, 1992).

The partitioning of noble gases from oil or water into the gas phase is a function of the solubility of the noble gases in the liquid phase, which, among other factors, depends on the atomic mass of the gas. Therefore, fractionation may occur if samples are collected from a separator. According to Ballentine et al. (1996), between 82 and 96% of He, Ne, and Ar, is transferred into the gas phase at the separator. This confirms that noble gases strongly partition into the gas phase, resulting in minimal isotopic fractionation during the steam separation process. Gas fields with high gas/(water+oil) ratios further reduce noble gas (elemental) fractionation during collection of the samples at the separator (Torgersen and Kennedy, 1999).

Mafic phenocrysts and xenoliths
Mafic minerals contained in volcanic rocks (phenocrysts) or in xenoliths are widely exploited in noble gas studies as they frequently contain fluid and/or melt inclusions which trap noble gases. Olivines and pyroxenes are the most commonly utilized minerals. Whole-rock samples are first crushed to 0.5 - 2 mm or larger, depending on the size of the crystals. The olivines and pyroxenes are then separated using a Frantz-Isodynamic magnet separator, followed by hand picking under a binocular microscope to remove any adhering matrix. Mineral separates are then cleaned in distilled water, methanol or acetone. After cleaning and drying, the separates can be processed for noble gases. The two extraction techniques generally used to decrepitate inclusions in the samples are vacuum crushing and vacuum melting. Both methods, however, integrate volatiles from all types and sizes of inclusions in the sample. The relatively recent application of lasers to noble gas studies of mafic crystals (e.g. Burnard et al., 1994) offers the exciting possibility that individual inclusions, or trails of inclusions, can be targeted to reveal spatial and/or temporal variations preserved within natural samples.

There are two general categories of crushing devices whereby crushing takes place either on-line or off-line (see Hilton et al., 1999 for a description of the two types of crusher and a comparison of He isotope results produced by both). In the case of on-line devices, vacuum is maintained between the crusher and the mass spectrometer inlet line during the crushing or pulverizing of the sample. This is not the case for off-line crushers. Indeed, many samples processed for He-isotopes prior to the early-mid 1990s were processed by off-line "ball mills": in these cases, careful monitoring of possible air leakage (e.g., by neon analysis) was deemed essential to ensure the integrity of the helium isotope results (e.g. Hilton et al., 1992). A further potential problem with off-line ball-mills relates to their exceptional efficiency in crushing samples. Prolonged crushing times of mafic crystals can lead to the release of He components extraneous to the magmatic system under scrutiny, e.g., cosmogenic and/or radiogenic He sited in the mineral matrix (Hilton et al., 1993a; Scarsi, 2000). Nowadays, most investigators use on-line crushing devices, with many adopting the added precaution of minimizing crushing times (Hilton et al., 1993a, 1999).

Submarine glasses
Submarine glasses from a variety of tectonic environments (including arcs and back-arcs) are a widely exploited medium for obtaining noble gas isotopic compositions and

abundances. The rapid quenching of lava exteriors as they are extruded onto the seafloor is assumed to trap volatile phases in the glassy rinds before they can be degassed. The normal procedure (e.g. Hilton et al., 1993b) involves selecting pristine, glass chips and shards by hand picking under a binocular microscope. Only glass pieces with either completely vitreous surfaces or no visible signs of alteration are selected for analysis. The glasses are then cleaned ultrasonically with acetone and/or distilled water to remove any adhering matrix and/or alteration phases. Sizes of glass chips generally range from 1 to 5 mm in diameter. As in the case of mafic minerals, samples can be processed by both vacuum melting and crushing.

Problematic issues of noble gas analysis
Given the wide range of potential sampling media available for noble gas studies and the various means of extracting the gases for analysis, it is instructive to scrutinize results to test the integrity of both a particular sampling medium as well as the methodology or experimental approach.

Mafic minerals (olivine and clinopyroxene) are widely used to gain insight into the helium isotope systematics of the magmatic source region. However, there are processes that may compromise the integrity of $^3He/^4He$ results obtained using mafic crystals. These principally relate to addition of extraneous (radiogenic) helium through interaction with pre-existing crust or wallrock. The following observations are pertinent in helping to recognise these effects:

- A correlation between measured $^3He/^4He$ ratio and helium content for co-genetic suites of samples may reveal late-stage addition of crustal (radiogenic) helium to helium-poor samples. Hilton et al. (1995) noted that He-poor crystals in some ocean-island phenocrysts had low $^3He/^4He$ ratios consistent with addition of radiogenic He. This observation is more likely observed in pyroxenes due to their higher diffusivity for helium compared with olivines (Trull and Kurz, 1993).
- Correlations between $^3He/^4He$ ratios and a magmatic differentiation index. For example, Gasparon et al. (1994) found lower $^3He/^4He$ ratios in more highly evolved phenocrysts (phenocrysts with a lower Mg #) from the Sunda arc, Indonesia.
- Isotopic disequilibrium between coexisting phenocryst pairs. Marty et al. (1994) reported higher $^3He/^4He$ ratios in olivine phenocrysts compared to pyroxene or hornblende for Mt. Etna volcano, an observation which is consistent with addition of late-stage, radiogenic or atmospheric helium. The same effect is seen in arc-related phenocrysts from the Lesser Antilles (Van Soest et al., 2002).

Submarine glasses can also exhibit noble gas variations depending on the method chosen for gas extraction. Crushing releases volatiles sited in vesicles whereas melting integrates vesicle gas and gas dissolved in the glass phase. Depending upon the degree of vesicularity, noble gases can fractionate from each other as a function of their relative solubilities in silicate melt (Carroll and Draper, 1994). A direct corollary of partitioning of noble gases between vesicle and melt is that the melt phase can become extremely depleted in noble gases. As a consequence, the isotopic composition of this residual gas

(in the magma/glass) may become susceptible to modification by addition of volatiles resulting from either radiogenic or nucleogenic reactions (e.g. magma ageing; Zindler and Hart, 1986). Alternatively, extraneous volatiles could be added to volatile-poor magma immediately prior to eruption thereby modifying a magmatic noble gas signature by one characteristic of crustal contamination (see Hilton et al., 1993a).

When comparing different sampling media directly, large differences in $^3He/^4He$ ratios have been observed. For example, at Cerro Negro volcano, Nicaragua, olivine phenocrysts erupted in 1992 have $^3He/^4He$ ratios of 3.5 ± 0.5 R_A (Fischer et al., 1999a) whereas fumarole gases collected days after the eruption have ratios of 6.8 R_A (Sano and Marty, 1995). An unreasonably high residence time of approximately 1 Myr is needed to lower $^3He/^4He$ ratios in the phenocrysts from 6.8 to 3.5 R_A assuming a magma U-content of 0.3 ppm and a He-content of 1.5×10^{-9} cm^3STP/g olivine (and a He partition coefficient of 0.008; Marty and Lussiez, 1993). This time period is much longer than the age of the Cerro Negro volcanic system (Fischer et al., 1999a). For this active volcanic system, therefore, the noble gas ratios of fumarolic discharges may be more representative of the present-day mantle source, with the 1992 activity erupting olivine phenocrysts having trapped helium from an earlier magmatic episode.

NOBLE GAS SYSTEMATICS OF ARC-RELATED VOLCANISM

The study of noble gases in arcs began with the seminal work of Mamyrin et al. (1969) who reported $^3He/^4He$ ratios greater than air for geothermal fluids from the Kurile Islands. This early observation of primordial (mantle-derived) ^3He in arc volcanoes has been confirmed by numerous subsequent studies (e.g. Craig et al., 1978; Sano and Wakita, 1985; Poreda and Craig, 1989) which have repeatedly emphasised the role of the mantle wedge in dominating the helium budget in the great majority of cases (the Banda arc of Indonesia being a notable exception – see below). It was also realised through noble gas studies that other contributors to the arc volatile inventory (the subducting slab and/or arc crust) could be traced through either the relative abundance of a major volatile phase to a noble gas or by the isotopic composition of a particular noble gas. An example of the former would be the high N_2/Ar ratios of island arcs tracing addition of slab-derived sedimentary N_2 to the source region (Matsuo et al., 1978; Kita et al., 1993): in the latter case, it has been argued that low $^3He/^4He$ ratios in the Andes indicate (upper) crustal additions to the volatile budget (Hilton et al., 1993a).

In this section, we review the noble gas systematics of arc-related volcanism worldwide. Helium isotope studies dominate because most arc products are erupted sub-aerially, and air contamination is a relatively minor (and correctable) problem for helium: this is not the case for Ne-Ar-Kr-Xe isotope systematics. Consequently, this section is weighted towards reporting observations of helium isotope variations in arc-related minerals and fluids. However, we summarize also the available database for neon, argon and xenon isotopes (to date krypton shows only air-like isotopic compositions). Finally, we consider the limited database of the relative abundances of the noble gases in arc-related products.

Helium isotope systematics of arc-related volcanism

At present, there are close to 1000 reported $^3He/^4He$ ratios from a variety of sampling media associated with arc-related volcanism. Table 1 summarizes the total He isotope database representing 26 individual arc segments worldwide (see Fig. 1 for locations). In this compilation, we focus our attention on the active arc only as detailed across-arc studies (e.g. Sano and Wakita, 1985) have long established the link between the presence of mantle-derived helium and the locus of magmatic activity. Furthermore, we include in Table 1 all analyses irrespective of sampling medium - the only exception is duplicate analyses of the same sample (in which case the highest value has been selected). We have made no attempt to choose 'representative' values for a particular volcanic system: all analyses irrespective of distance from volcano summit (geothermal fluids) or age of lava flow (phenocrysts) are included. However, it should be noted that there is evidence of a geographic control on geothermal fluid $^3He/^4He$ ratios located around some individual volcanic centres: the highest values are found close to the eruptive vents and lower, more radiogenic values occur away from the volcanic centres (Sano et al., 1984; Williams et al., 1987; Marty et al., 1989; Hilton et al., 1993a; Van Soest et al., 1998). To facilitate discussion, we tabulate the range of $^3He/^4He$ ratios (maximum and minimum values) together with the average value (with 1 standard deviation from the mean). With reference to Table 1, the following points are emphasized:

- The highest arc-related ^{3}He/^{4}He ratios fall within the range normally associated with depleted (N-type) MORB mantle (i.e., $8 \pm 1R_A$; see Farley and Neroda, 1998 and Graham, 2002, this volume). The highest values ($8.8 - 8.9 \ R_A$) are reported for 4 arc segments: the southern Lesser Antilles (Pedroni et al., 1999), the Colombian Andes (Sano et al., 1997) and the Sunda arc system in both Sumatra (Gasparon et al., 1994) and Bali (Hilton and Craig, 1989).
- In nine of the arc segments, the highest ^{3}He/^{4}He ratio fails to reach the lower limit of the MORB range i.e. the highest value is less than $7R_A$. These segments are: 4 regions of the Andes (central and northern Chile, Peru and Equador), Kamchatka, the Kuriles and Taiwan (where the total number of samples is low), the eastern Sunda/Banda arc and the Campanian Magmatic Province of Italy (which both have unique tectonic arrangement of plates – see below).
- The lowest arc-related ^{3}He/^{4}He ratio ($0.01 \ R_A$) is found at the transition between the east Sunda and Banda arcs in Indonesia (Hilton et al., 1992). Other arc segments with low ^{3}He/^{4}He ratios ($< 1R_A$) are: the Chilean Andes (Hilton et al., 1993a), Colombia (Williams et al., 1987) and the Campanian Magmatic Province of Italy (Graham et al., 1993). Therefore, in a relatively small number of samples from these localities, radiogenic helium (with ^{3}He/^{4}He ratios $\sim 0.05 \ R_A$; see Andrews, 1985) predominates over any magmatic helium input.
- The mean ^{3}He/^{4}He ratio of arc-related volcanism is $5.4 \pm 1.9 \ R_A$ (all arc segments). Although the significance of the mean value is unclear – it does not possess the significance of an individual maximum or minimum ratio for example - it is noteworthy that only the east Sunda/Banda arc, the Campanian Magmatic Province and 3 segments of the Andes (northern Chile, Peru and Equador) have average ^{3}He/^{4}He ratios which are more than one standard deviation displaced from the global mean. These are the segments which have the lowest absolute ^{3}He/^{4}He ratios (see above point).

The general picture that emerges from the He-isotope compilation is that in most cases arc-related volcanism samples helium with an isotopic composition close to that found in MORB, i.e. that emitted at divergent plate boundaries. This observation was made very early in the history of helium isotope studies of arc-related volcanism (e.g. Craig et al., 1978), and still stands today in light of the much more extensive database (Table 1). The first-order implication of this observation is that the helium in the majority of arcs is predominantly of mantle derivation, and presumably derived from the mantle wedge. This point can be illustrated by taking the mean global ^{3}He/^{4}He ratio calculated in Table 1 ($5.4R_A$) and assuming that it represents a two-component mixture of MORB-type ($8R_A$) and radiogenic ($0.05R_A$) helium. In this case, approximately 67% (or two-thirds of the helium) is MORB-type helium and derived from the mantle wedge. Clearly, the proportion increases (up to 100% in some cases) for those samples with ^{3}He/^{4}He ratios higher than the mean value.

Considerable debate has arisen as to the (ultimate) origin of the high ^{3}He/^{4}He ratios typical of mantle-derived material in arcs and elsewhere. Anderson (1993) questioned the widely held notion that high ^{3}He/^{4}He ratios result from retention of primordial helium in

the mantle and/or core with time-integrated lowering of the ratio by addition of ^{4}He produced from radioactive decay. As an alterative, he suggested subduction of marine sediments rich in IDPs (interplanetary dust particles) as the source of mantle ^{3}He. This suggestion has been criticised both because the rate of IDP deposition is orders of magnitude too low to sustain the flux of mantle ^{3}He at ridges (Trull, 1994), and because the diffusivity of helium is too high in IDPs for effective retention from the sediment-ocean interface to mantle P-T conditions (Hiyagon, 1994). Hilton et al. (1992) has also presented arguments against subducting sediments acting as a transport medium for helium into the mantle based on its high diffusivity in various sediment-hosted minerals. Therefore, high ^{3}He/^{4}He ratios in mantle-derived samples are still viewed as reflecting mixing between primordial volatiles, captured during Earth accretion, and radiogenic helium produced throughout Earth history (see also Porcelli and Ballentine, 2002, this volume).

Debate has also arisen regarding the origin of the small but discernible contribution of radiogenic helium found in arcs with predominantly mantle helium isotope signatures. On the one hand, radiogenic helium could result from the subduction process, and be associated with the subducted slab – either the sedimentary veneer or the underlying oceanic basement. On the other hand, the arc lithosphere through which magmas are erupted could provide the radiogenic helium, and thus lower resultant ^{3}He/^{4}He ratios in samples at relatively shallow levels. As discussed above, we consider the high diffusivity of helium in sedimentary material to be a persuasive argument against the subduction of helium into the mantle (Hilton et al., 1992; Higayon, 1994). Furthermore, a comparison of the output flux of helium via arcs compared to the input flux (via the trench) shows that even when crystalline (basaltic) basement is considered, possible subduction of helium cannot support the return flux from the mantle (see section: Volatile mass balance at subduction zones). Circumstantial evidence also tends to implicate crustal contamination. For example, arc segments with significant volumes of subducting sediments (Alaska, the Aleutian Islands, Java, New Zealand; Table 1) and/or old oceanic basement (western Pacific arcs: Japan, the Marianas, Java; Table 1) have ^{3}He/^{4}He ratios which fall within the canonical MORB-He isotope range of $8 \pm 1R_A$ suggesting little or no slab influence. In contrast, ^{3}He/^{4}He ratios < 7 R_A are observed more commonly in those arc segments which erupt through thickened crust of continental affinity (e.g., Taiwan, Kamchatka, the Andes – with the exception of Colombia; Table 1). For these reasons, we favour the hypothesis that the arc crust and/or lithosphere are responsible for the addition of radiogenic helium (see also discussion in Porcelli et al., 1992; Hilton et al., 1993).

In addition to the majority of arcs with predominantly mantle-derived helium, there are 3 segments which stand out as emitting helium with ^{3}He/^{4}He values consistently lower than the MORB range: the east Sunda/Banda arc of eastern Indonesia, the Campanian Magmatic Province of Italy and the Andes – particularly the Chilean segments. These arc systems are clearly unusual, at least in terms of their He-isotope systematics, and merit further comment.

East Sunda/Banda Arc. The eastern section of the Sunda arc and the contiguous Banda arc was the first arc system where predominantly radiogenic helium was found to characterise volcanic emissions (Poreda and Craig, 1989). In this region, $^3He/^4He$ ratios reflect the overwhelming influence of radiogenic helium in the source region - a remarkable departure from observations at other western Pacific arcs. The transition from normal 'arc-like' ratios (6-8 R_A) to the predominantly radiogenic helium values ($\leq$ 1-2 R_A) is centred on the island of Flores in the eastern Sunda arc and is extremely sharp (Hilton and Craig, 1989; Hilton et al., 1992). It coincides with the change in composition of the subducting slab from normal oceanic lithosphere in the Sunda arc located to the west, to crust of continental affinity in the east - the leading edge of the Australian continental margin as it is subducted beneath the Banda Sea. The transition in type of subducting crust is traced with remarkable clarity in He-isotope space whereas other isotopic systems (e.g., $^{87}Sr/^{86}Sr$) display only a broad gradual change through the transition region (Hilton and Craig, 1989). In this unusual tectonic environment, therefore, we see one of the rare examples where the effect of radiogenic helium associated with the subducting slab is discernible through the MORB-like helium signal normally associated with the mantle wedge.

Southern Italy. There is a pronounced northward decrease in $^3He/^4He$ ratios between the Aeolian Islands of southern Italy and the region of Mt. Vesuvius known as the Campanian Magmatic Province or the Neopolitan volcanic region. Mt. Etna on Sicily can be included in this trend as recent work (e.g. Schiano et al., 2001) indicates a progressive transition from a plume-related to a typical island-arc source for this volcano. The trend or 'step function' in the helium isotope systematics of southern Italy was first pointed out by Sano et al. (1989) and ascribed to shallow crustal contamination effects. However, subsequent work (Marty et al., 1994) has shown the combined He-O-Sr-C isotope systematics are consistent with the progressive involvement of Africa continental crust which has been subducted beneath the southern Tyrrhenian Sea. The influence of the African plate increases in a northerly direction (Marty et al., 1994) - towards Mt. Vesuvius (see data of Graham et al., 1993) and possibly as far north as the Roman and South Tuscany volcanic provinces (see Tedesco, 1997).

The Andes. In the Chilean Andes, high (5-7 R_A) and low (< 1 R_A) helium isotope ratios occur in both the Central and Southern Volcanic Zones (Hilton et al., 1993a). In contrast to the east Sunda/Banda arcs, there appears to be no spatial control on the distribution of $^3He/^4He$ ratios, nor any correlation between $^3He/^4He$ and Sr (or Pb) isotopes – an observation used to rule out a slab origin for the radiogenic helium isotope signal. Instead, it has been suggested that the principal control on the measured $^3He/^4He$ values is a combination of near surface magmatic degassing and crustal contamination of degassed magmas. It is noteworthy, however, that the highest $^3He/^4He$ ratios in each volcanic zone fall short of the MORB range (6.9 R_A in the Southern Zone and 6.0 R_A in the Central Zone) leading to the suggestion (Hilton et al., 1993a) that the magmatic base-line in $^3He/^4He$ ratios is set by assimilation processes in the lowermost crust (MASH zones; Hildreth and Moorbath, 1988) prior to transfer of magma towards the surface.

Neon and argon isotope systematics of arc-related volcanism
In contrast to the extensive helium isotope database described above, there are relatively few argon (n ~260) and even fewer neon (n < 100) isotope analyses available for arc-related samples. The available data are summarized in Table 2 (neon) and Table 3 (argon), adopting the same format as the helium isotope database. In the cases of neon and argon, however, reported isotope results invariably reflect varying degrees of contamination with air as a consequence of both the low intrinsic concentrations of these volatiles in natural samples and their greater abundance (relative to helium) in air. Therefore, more significance could be given to the extreme (higher) values as they represent samples least affected by air contamination.

In Figure 2 we plot arc-related neon isotope ratios on the traditional 3-isotope neon plot using only those samples (n = 34) with reported $^{20}Ne/^{22}Ne$ and $^{21}Ne/^{22}Ne$ ratios that are distinct from the air value (at the 1 sigma level). The data appear to follow three trends:
- Samples from all 5 arc regions plotted have values which lie along the so-called MORB-trend (Sarda et al., 1988; Graham, 2002, this volume). This is most convincingly seen for samples from the Aeolian arc (Etna region; Nakai et al., 1997) and, to a lesser extent, New Zealand (Patterson et al., 1994).
- Fumarole gases from Vulcano (Aeolian arc) and Vesuvius (Campanian Magmatic Provence) have radiogenic neon (i.e., neon enriched in ^{21}Ne and, to a lesser extent, ^{22}Ne) and follow the trajectory labelled 'Crustal-neon'. To date, this observation is unique to Italian volcanism and has been attributed to the influence of nucleogenic neon produced in (subducted) crustal material (Tedesco and Nagao, 1996; Tedesco et al., 1998).
- All arc regions have samples with neon isotope ratios overlapping with the mass fractionation line (mfl). No petrogenetic significance is attached to these observations as they are probably related to degassing phenomena.

Samples lying along the MORB-trend in 3-isotope neon space can be interpreted as tapping a mantle source (the mantle wedge). For the most part, the $^3He/^4He$ ratios of the same samples are MORB-like, or close to MORB, indicating a common origin for both light noble gases. In this respect, the helium and neon isotope systematics are coupled (within error) as postulated by the solar neon hypothesis (Honda et al., 1993a; see also Graham, 2002, this volume). In contrast, samples that lie along the crustal-neon trajectory (Fig. 2) present an extreme example of helium-neon decoupling. According to the solar neon hypothesis, samples with 'crustal' neon should also be characterized by radiogenic helium (< $0.1R_A$) given that nucleogenic ^{21}Ne and radiogenic ^4He are produced at a constant ratio ($^{21}Ne/^4He$ = 4.5 x 10^{-8}; Yatsevich and Honda, 1997). However, samples from Vulcano and Vesuvius lying on the crustal neon trajectory (with $^{21}Ne/^{22}Ne$ ratios > 0.035) have $^3He/^4He$ ratios in the range 7.5-7.7 R_A (Vulcano, Aeolian arc; Tedesco and Nagao, 1996) and 2.1-3.4 R_A (Vesuvius, Campian Magmatic Provence; Tedesco et al., 1998). In both cases, neon seems to originate overwhelmingly from a crustal source yet a significant fraction of the helium (almost 100% in the case of Vulcano) is of mantle derivation. A satisfactory explanation for this apparent He-Ne decoupling has still to emerge.

The argon isotope database for arcs (Table 3) shows $^{40}Ar/^{36}Ar$ ratios to be significantly lower than values found for MORB ($^{40}Ar/^{36}Ar$ > 40,000; Burnard et al., 1997). The highest values in arc-related terrains are reported for Vulcano, Italy ($^{40}Ar/^{36}Ar$ = 2,082; Magro and Pennisi, 1991) and New Zealand ($^{40}Ar/^{36}Ar$ = 1,160; Patterson et al., 1994). Other localities show less enrichment in radiogenic argon-40 with a large proportion of samples having $^{40}Ar/^{36}Ar$ ratios close to the atmospheric value (mean ratios in Table 3 fall close to 296). Most interpretations of the argon isotope database call for overwhelming addition of air-like argon: however, debate centres on its origin. For example, Marty et al. (1994) suggest that air-like argon reflects assimilation processes between magmas and surrounding (crustal) wallrock permeated with air-like argon whereas Tedesco et al. (1998) call for the argon to be recycled from the subducted slab. An intriguing correlation between ^3He and ^{36}Ar in olivines and whole rocks from the Horoman ultramafic complex in Japan (Matsumoto et al., 2001) further suggests that atmospheric argon in these samples is recycled from the subducted slab. In the case of geothermal fluids, recharging meteoric waters and/or contamination during sampling seems an obvious means to introduce air-derived argon.

The origin of the radiogenic argon is more problematic as both mantle and crustal reservoirs are characterized by high $^{40}Ar/^{36}Ar$ ratios. Kennedy et al. (1991) attributed radiogenic ^{40}Ar in Honduran geothermal fluids to a crustal source based upon measured $^3He/^{40}Ar*$ ratios (where $^{40}Ar*$ represents 'radiogenic' ^{40}Ar added to air-like argon to increase the $^{40}Ar/^{36}Ar$ ratio) which were typically 20 times less than MORB values. Other authors (e.g., Patterson et al., 1994) have attempted to scale the radiogenic argon to the contribution of radiogenic ^4He (from the crust). Based on the fact that most arc-related $^3He/^4He$ ratios are close to the MORB value, i.e., the contribution of crustal ^4He is relatively small (see Table 1), most of the radiogenic ^{40}Ar is then attributed to the mantle wedge.

To date, there is no convincing evidence in the arc-related database that $^{38}Ar/^{36}Ar$ ratios deviate significantly from the air value except in cases of mass fractionation (Nagao et al., 1981).

Krypton and xenon isotope systematics of arc-related volcanism
There are no reports of krypton isotope anomalies in arc-related terrains – the small number of krypton isotopic analyses (e.g., Patterson et al., 1994) reveal only atmospheric-like ratios. For the most part, the situation is similar for xenon – atmospheric-like ratios dominate the few analyses reported. An exception is found in the work of Nakai et al. (1997) which reports 2 samples from the vicinity of Mt. Etna with enrichments in both ^{129}Xe and ^{136}Xe relative to air. The anomalies are correlated such that they appear to reflect mixing between air and an enriched source with a xenon isotope signature similar to MORB.

Relative noble gas abundance systematics of arc-related volcanism

Patterns of relative noble gas abundances are usually reported in the $F_{(m)}$ notation where $F_m = (^mX/^{36}Ar)/(^mX/^{36}Ar)_{atm}$ where ^mX represents a noble gas element X of mass m. Data are available from the following arc segments: Japan (Matsubayashi et al., 1978; Nagao et al., 1981), New Zealand (Marty and Giggenbach, 1990; Patterson et al., 1994), Central America (Kennedy et al., 1991) and the Aeolian arc (Nakai et al., 1997; Tedesco and Nagao, 1996). Irrespective of sampling medium (phenocryst or geothermal fluids) there appear to be a number of common features in the relative noble gas abundance patterns of arc-related samples:

- Extreme enrichments in helium (both ^{3}He and ^{4}He) compared to air. For example, Patterson et al. (1994) report a maximum F_3 value of ~22,000 for New Zealand phenocrysts while Kennedy et al. (1991) found a maximum F_4 of 107 for Honduras geothermal fluids. Based on the ^{3}He/^{4}He ratio of the helium, the enrichment is usually attributed to the input of magmatic gas originating in the mantle wedge.

- F_{Ne} and F_{Kr} values which resemble air or the noble gas abundances of air-saturated water (asw) i.e., $F_{Ne} < 1$ and $F_{Kr} > 1$. In the case of geothermal fluids, slight differences from the actual air or asw values have been ascribed to either uncertainties in the recharge temperature of the fluids or to fractionation processes associated with either vapour-phase separation or bubble formation (e.g., Kennedy et al., 1991). In the case of phenocrysts (e.g. from New Zealand), Patterson et al. (1994) explained the variations in F_{Ne} and F_{Kr} about the atmospheric values by solubility-controlled elemental fractionation associated with mass transfer between basaltic melt and a distinct vapour phase.

- Significant enrichments in F_{Xe}. F_{132} values as high as 7.3 have been reported for both phenocrysts (Patterson et al., 1994) and geothermal fluids (Kennedy et al., 1991). This is greater than values anticipated by either vapour-magma models or by fractionating asw respectively. It has been suggested that adsorption-desorption processes, possibly associated with host rocks, could create such a xenon-rich component (see Marty and Giggenbach, 1990).

NOBLE GASES IN BACK-ARC BASINS

The majority of back-arc basins are formed by extension and seafloor spreading behind, or within, an island arc: their formation is, therefore, associated with contemporaneous subduction-zone activity (Saunders and Tarney, 1991). From the earliest geochemical studies of back-arc basin basalts (BABB) (e.g. Hart et al., 1972; Hawkins, 1976; Gill, 1976; Tarney et al., 1977) it has been recognised that although similar to MORB - in mineralogy and major chemistry - BABB were enriched in large ion lithophile (LIL) trace elements such as Ba compared to high field strength (HFS) elements like Ti and Zr. Differences in trace element geochemistry extend also to volatile compositions: for the most part, BABB have higher volatile contents - particularly water. In part, the higher water (and other volatile) contents of some BABB result from the propensity of back-arc basins to erupt more evolved magma types and the fact that water acts incompatibly during fractionation. However, it is apparent when comparing BABB with MORB at equivalent TiO_2 or MgO contents that BABB still have higher absolute volatile contents. This observation has been taken as evidence that back-arc basin lavas contain a volatile

component originating from the associated subducting slab. For this reason, they provide insights complementary to those from arc volcanism on the topic of noble gases in subduction zones.

Helium isotopes in back-arc basins
In Table 4 we summarize the available helium isotope data for back-arc basins (see Fig. 1 for locations). For the most part, the database has been obtained using vacuum crushing techniques on glass rinds of pillow lavas – therefore, the helium is representative of the vesicle phase of such samples. A notable exception is the study by Ishibashi et al. (1994) who measured $^3He/^4He$ ratios in hydrothermal fluids from the North Fiji Basin. Comparisons of $^3He/^4He$ ratios between oceanic glasses and hydrothermal fluids (e.g. at Loihi Seamount; Hilton et al., 1998) indicate that both sampling media provide valuable means of obtaining He isotope information on underlying magma sources.

Helium isotope ratios at the four back-arc basins studied to date cover almost the complete range observed in the terrestrial environment (excluding samples containing cosmogenic ^3He; see Niedermann, 2002, this volume). $^3He/^4He$ ratios > MORB (i.e. higher than 8 ± 1 R_A) are observed at 3 of the back-arc basins: the Manus Basin (15.2 R_A), the Lau Basin (22.1 R_A) and the North Fiji Basin (10.3 R_A). Such high values are normally considered diagnostic of a deep-seated mantle plume component (Craig and Lupton, 1976), and the respective authors in the three cases above have adhered to this interpretation. For example, Poreda (1985) and Poreda & Craig (1992) suggested that channelling of plume material from the nearby Samoa hotspot could explain the $^3He/^4He$ ratios at Rochambeau Bank towards the northern end of the Lau Basin (see Turner and Hawkesworth (1998) for further discussion on mantle flow between Samoa and the Lau Basin). Similarly, Macpherson et al. (1998) explained high $^3He/^4He$ ratios in the Manus Basin as reflecting a mantle plume originating at the underlying core-mantle boundary. While noting the presence of a "^3He-rich, hotspot-like component" in the North Fiji Basin, Ishibashi et al. (1994) did not comment on its specific origin. In all three cases, however, there was no attempt to relate the high $^3He/^4He$ ratios to shallow processes associated with the back-arc, so it appears safe to assume that the high values observed in these regions bear little or no information on the subduction process.

Whereas the majority of the Manus Basin samples (particularly from the Manus Spreading Centre and the Extensional Transform Zone) are characterized by $^3He/^4He$ ratios greater than those of MORB, this is not the case for lavas from the Lau Basin or the North Fiji Basin. Indeed, a significant number of samples from both basins have MORB-like $^3He/^4He$ values (see references in Table 4). Specifically, lavas with $^3He/^4He$ values of 8 ± 1 R_A are erupted in the central Lau Basin as well as along all spreading centres of the North Fiji Basin. Therefore, in addition to a contribution from a deep mantle plume, the other principal source of helium in active back-arc basins is the same as that supplying mid-ocean ridges. This conclusion reinforces that derived from the majority of island arc studies - namely, that the mantle is the predominant source of helium in subduction zone environments with little or no contribution from the subducted slab.

There are, however, a number of samples in each of the four back-arc basins that have $^3He/^4He$ values significantly lower than the MORB range. Oceanic glasses with $^3He/^4He$ ratios ≤ 1 R_A (implying that ≥ 80% of the helium is radiogenic in origin; Andrews, 1985) are observed along the Peggy Ridge and Valu Fa Ridge (Lau Basin), the central Mariana Trough and throughout the Manus Basin (Table 4). Assuming that, in all cases, the glasses used in these studies were (a) young enough to rule out post-eruptive in-growth of ^4He, and (b) pristine in condition to exclude seawater contamination, then any radiogenic helium must have been inherited prior to eruption of the lavas onto the sea floor. Three explanations have been advanced to account for the occurrence of these low $^3He/^4He$ values:

- The mantle wedge is depleted in helium so that it cannot mask (dilute) radiogenic helium derived from the subducted slab (subducted sediments or underlying oceanic basement).
- Magmas are contaminated by radiogenic helium trapped in crust through which the magmas are erupted. Contamination is accentuated by pre-eruptive degassing of magmas which lowers absolute concentrations thereby making magmas more susceptible to contamination.
- The mantle wedge is enriched in U- and Th- series isotopes derived from the subducted slab so that the wedge itself is characterized by $^3He/^4He$ ratios < MORB.

The first explanation was suggested by Poreda (1985) to explain a small number of low $^3He/^4He$ ratios (<< MORB) at various localities in the Mariana Trough. By invoking a low concentration of mantle wedge helium, presumably caused by extensive degassing, it should be possible to observe the effects of the addition of slab-derived radiogenic helium on resultant $^3He/^4He$ ratios. In this way, Poreda (1985) reconciled the observation of low $^3He/^4He$ ratios with the high (and isotopically heavy: δD ~ -40 ‰) water and alkali contents which frequently characterise BABB lavas. Hilton et al. (1993b) re-interpreted the Mariana Trough data in terms of degassing of mantle-derived melts prior to assimilation of hydrated minerals and/or other alteration products in older oceanic crust (arc basement) immediately prior to eruption (second explanation above). This scenario is consistent with both the anticipated D/H and $^3He/^4He$ signature of upper crustal materials. This interpretation follows from observations of low $^3He/^4He$ ratios (and low helium contents) of differentiated lavas erupted along the Valu Fa Ridge (Lau Basin). The low helium contents make such samples susceptible to any assimilation and/or contamination effects. Bach and Niedermann (1998) challenged this (degassing-contamination) interpretation suggesting that the mantle wedge (in the Valu Fa region) is both depleted in mantle helium and metasomatised by slab-derived fluids introducing U and Th (third explanation). Therefore, over time, it would have evolved to a $^3He/^4He$ ratio slightly lower than that of MORB. Clearly, observations of back-arc basin $^3He/^4He$ ratios less than those found in MORB represent a contentious issue in noble gas isotope geochemistry with far-reaching implications for questions such as whether helium can be subducted, and how the volatile content of the mantle wedge has evolved. As more BABB helium data is produced, debate is likely to continue regarding the relative merits of these three possibilities.

Neon isotopes in back-arc basins

In contrast (again) to the helium isotope database, neon data in BABB are sparse. To date, neon isotope results are available for the Lau Basin (Honda et al., 1993b), the Mariana Trough (Ikeda et al., 1998; Sano et al., 1998a) and the Manus Basin (Shaw et al., 2001). In Figure 3, we plot the complete database in the traditional 3-isotope neon plot. There are three points to note:

- Most samples from the Mariana Trough (with the exception of one outlier) plot close to the MORB correlation line.
- The Lau Basin data lie on a linear trajectory slightly steeper than the MORB-line but nowhere near the Loihi-Kilauea (L-K) correlation lines. One sample from the Mariana Trough (which has the most extreme enrichments in $^{20}Ne/^{22}Ne$ and $^{21}Ne/^{22}Ne$ of the entire database) also appears to lie along the same trajectory.
- The Manus Basin samples lie along a trajectory with a slope less than the MORB correlation line (the so-called 'Manus trend').

As all samples appear to follow linear trajectories in 3-isotope neon space, they must represent binary mixtures between two endmembers with distinct neon isotope systematics. One endmember is clearly air reflecting the inevitable contamination of all terrestrial samples with atmospheric neon. The other endmember consists predominantly of 'mantle neon' which is itself composed of a mixture of solar neon (high $^{20}Ne/^{22}Ne$ ~ 13.8) and nucleogenic neon (high $^{21}Ne/^{22}Ne$) – in various proportions.

According to the solar-neon hypothesis (Honda et al., 1993a), helium and neon isotopes are coupled and reflect addition of radiogenic ^4He and nucleogenic ^{21}Ne, continuously produced throughout Earth history, to primordial He and Ne captured at the time of planetary accretion. Therefore, the predicted $^3He/^4He$ ratio of those samples lying along the MORB neon correlation line is 8 R_A. The fact that the Mariana Trough samples all fall within error of the MORB $^3He/^4He$ ratio substantiates the solar-neon hypothesis and indicates negligible input of helium and neon from any reservoir other than the mantle wedge.

In the case of the Lau Basin, Honda et al. (1993b) showed that samples from the Central Spreading Center had measured $^3He/^4He$ ratios (8 ± 1 R_A) in agreement with predictions from the solar neon hypothesis and the observed neon isotope values i.e. the trajectory in Figure 3 (slightly steeper than the MORB line) predicts a $^3He/^4He$ ratio of 8.6 R_A – within error of observed values. In this respect, the source of the noble gases (He and Ne) in this part of the basin was solely the mantle wedge. This was not the case for the King's Triple Junction in the north section of the Lau Basin. Here, measured $^3He/^4He$ ratios (5.9 – 7.4 R_A) were less than those predicted from neon isotope systematics (8.6 R_A) leading to the suggestion of a (radiogenic) helium contribution from the slab (without any concomitant neon addition). Note that Hilton et al. (1993b) also measured a 'low' $^3He/^4He$ ratio (6.9 R_A) in this part of the basin and ascribed it to pre-eruptive degassing of mantle-derived helium followed by contamination by crustal helium.

For the Manus Basin, Shaw et al., (2001) reported the unusual occurrence of highly nucleogenic neon isotope ratios (trajectory less steep than that of MORB – Fig. 3) together with plume-like ^{3}He/^{4}He values. ^{3}He/^{4}He ratios ~12-15 R_A for the Manus Basin would predict a trajectory in neon isotope space close to the L-K line. This unique decoupling of helium-neon isotope systematics was ascribed to a highly fractionated (i.e. high He/Ne) source region resulting from either prior plume degassing - followed by in-growth, or to mantle heterogeneity inherited from the accretion process (Shaw et al., 2001). Significantly, no evidence was found to support the subducting slab, either the present-day Solomon Sea plate or ancient recycled slab, as a potential source of the nucleogenic neon (Shaw et al., 2001).

In summary, therefore, there is little or no firm evidence from neon isotopes, either taken alone or when considered along with He isotopes, for a significant input of slab-derived volatiles to back-arc basin lavas.

Argon, krypton and xenon isotopes in back-arc basins
Non-atmospheric ^{40}Ar/^{36}Ar ratios are found in all 4 back-arc basins considered above (Table 5). The highest ratio (5300) is reported for the northern section of the Lau Basin (Honda et al., 1993b) but the other three basins (Mariana Trough, North Fiji Basin and the Manus Basin) all have ^{40}Ar/^{36}Ar values > 1000. There appears consensus on the origin of the high ratios – namely, the mantle wedge, even though the absolute ratios fall far short of MORB-type values (up to 40,000; Burnard et al., 1997). This relatively narrow range in ^{40}Ar/^{36}Ar ratios for BABB (296 – 5000) reflects the ubiquitous presence of air-derived argon in all samples, which acts to lower values until they converge on ^{40}Ar/^{36}Ar ratios ~296 indicating the overwhelming dominance by an air-derived component. Debate on the origin of the low ^{40}Ar/^{36}Ar ratios in back-arc basins (subduction-related or upper crustal contamination) mirrors that for arc localities.

As all samples in Table 5 are oceanic glasses, and therefore erupted in a submarine setting, the most pressing concern is seawater contamination. Honda et al. (1993b) noted a correlation between absolute abundances of krypton and xenon (which are relatively enriched in seawater) with total water content, and suggested interaction with seawater as one possible explanation for the atmospheric-like heavy noble gas systematics. They also pointed to a correlation between Kr and Xe and Ba/Nb ratio (a key slab fluid tracer), opening up the possibility that seawater interaction may have occurred in the down-going slab and not necessarily close to the site of eruption. In this way, the heavy noble gases (and by implication the low ^{40}Ar/^{36}Ar ratios) would be indicative of volatiles recycled through the subduction zone. Bach and Niedermann (1998) have also taken up this point as they observed the same type of correlations between absolute abundances of noble gases and both water contents and Ba/Nb ratios for samples from the Valu Fa Ridge (Lau Basin). The alternative explanation, that low ^{40}Ar/^{36}Ar ratios in back-arc basins trace shallow-level contamination of arc-rifted crust, was advanced by Hilton et al. (1993b) who argued that such crust has the necessary attributes of radiogenic He, low ^{4}He/^{40}Ar* values (where ^{40}Ar* is radiogenic argon) and low ^{40}Ar/^{36}Ar ratios (~ 300) resulting from ageing and modification by hydrothermal alteration. Interaction of previously-degassed

primary magmas with such crust would result in the superimposition of a slab-like signature (high water, high Ba/Nb) onto crustal noble gases characteristics, and result in geochemical features such as seen along the Valu Fa Ridge. As in the case of argon isotope variations in arc-related volcanism, considerable controversy still surrounds assigning provenance to potential endmember contributors.

Finally, we note that deviations from atmospheric-like krypton isotope ratios have not been found for any back-arc basin: however, there are two reports of anomalous xenon isotope variations for the Mariana Trough. Ikeda et al. (1998) found coupled $^{134}Xe/^{130}Xe$ and $^{129}Xe/^{130}Xe$ deviations from air - similar to those found in MORB, whereas Sano et al. (1998a) reported only ^{129}Xe excesses (relative to ^{132}Xe). These signatures reinforce the idea that the mantle wedge is the principal source of volatiles in the Mariana Trough particularly where circumstances limit the amount of atmosphere-derived contributions. At all other localities, only atmospheric-like xenon isotope ratios have been found.

RECYCLING OF VOLATILES AT SUBDUCTION ZONES: A MASS BALANCE APPROACH

In the previous two sections, we considered the noble gas systematics of arc and back-arc regions. We now turn our attention to the exploitation of the noble gases in understanding volatile mass balance at subduction zones. Our focus is on the ability of noble gases to both quantify mantle-degassing rates and identify volatiles of differing provenance. Specifically, we discuss the utility of noble gases in determining the volatile output via subduction zones from various sources – both the intrinsic output of noble gases themselves as well as the other (major) volatile phases which comprise the terrestrial atmosphere.

In addition, we adopt a new approach to calculate volatile outputs for individual arc segments worldwide. This allows us to assess the volatile mass balance for a number of convergent margins worldwide. In this way, we can determine more realistically how the range in volatile input parameters affect volatile output. Summing the input versus output parameters globally, we consider the long-term recycling efficiency of both the major volatiles and the noble gases, and discuss implications for Earth evolution.

The global volatile output at arc volcanoes – the ^{3}He approach

There have been numerous attempts at estimating volatile fluxes associated with arc-related volcanism. In this respect, the noble gas isotope that has received most attention is ^{3}He as its primordial origin makes it an unambiguous tracer of mantle-derived volatiles. Therefore, if the arc flux of ^{3}He can be established, it would lead to the derivation of other volatile fluxes by simple measurement of the ratio $x_i/^3He$, where x_i is any volatile species discharging from volcanoes (CO_2, SO_2, H_2S, HCl, N_2, etc.). Two distinct approaches have been taken to estimate the ^{3}He flux from arc volcanoes:

- Using the relatively well constrained figure of mid-ocean ridge degassing flux (~1000 mol^{3}He/yr; Craig et al. 1975), together with the assumption that the magma production rate of arcs is 20% that of MOR (Crisp, 1984), an arc ^{3}He flux of ~200 ± 40 mol/yr is derived (Torgersen, 1989). This method further assumes

that the ^{3}He content of magma in the mantle wedge is the same as that beneath spreading ridges.

- Using total ^{3}He fluxes calculated for subaerial volcanism and estimating the fraction contributed by arc volcanism. For example, Allard (1992) derived an estimate for the total flux of ^{3}He into the atmosphere by subaerial volcanism to be 240-310 moles/yr (based upon integrating the CO_2 flux from 23 individual volcanoes worldwide and coupling this flux with measurements of the $CO_2/^3$He ratios). Of the total subaerial ^{3}He flux, he suggested that approximately 70 mol/yr was arc-related. Adopting a similar approach, Marty and LeCloarec (1992) used polonium-210 (^{210}Po) as the flux indicator (along with the ^{210}Po/^{3}He ratio) to estimate a total subaerial volcanic ^{3}He flux of 150 mol/yr – of which over half (> 75 mol/yr) was due to arc volcanism.

It should be noted that neither approach attempts a direct measurement of the arc ^{3}He flux. Whereas scaling to estimated magma production rates is used in the first instance, the second methodology relies on knowledge of an absolute flux of some chemical species from volcanoes together with a measurement of the ratio of that species to ^{3}He. The most widely used species to derive absolute chemical fluxes from subaerial volcanoes is SO_2 using the correlation spectrometer technique (COSPEC) (Stoiber et al., 1983). Carbon dioxide (see Brantley and Koepenick, 1995) as well as ^{210}Po (Marty and LeCloarec, 1992) have also been used to calibrate absolute fluxes of other species albeit to a much lesser extent.

In Table 6, we compile various estimates of the volatile flux from arcs for a number of noble gas isotopes (^{3}He, ^{4}He and ^{36}Ar) and major volatile phases (N$_2$, CO_2 and H_2O). The reader is referred to the literature given in the footnote for details of the methodology adopted to derive each estimate and the inherent assumptions involved. For comparison, we also compile estimates of the total subaerial volcanic fluxes. Note that all flux estimates in Table 6 are made on a global basis, i.e. the fluxes are assumed to represent the integrated output from all arcs worldwide. Although such fluxes are essential in addressing large-scale geochemical questions (e.g., mass transfer of volatiles through the upper mantle; Porcelli and Wasserburg, 1995), they are of limited use in assessing the state of mass balance (input via the subducting slab versus output via the arc and back-arc) at individual arcs worldwide, and the (localized) effect of variations in the type and amount of subducted sediment on volatile output. For these questions, an estimate of volatile fluxes at individual arc segments is required. In the next section, we adopt an integrated flux approach (using SO_2) to produce volatile flux estimates but limit ourselves to distinct arc segments. A test of the success of this approach will be whether the sum of the individual arc fluxes equals that derived on a global basis (Table 6).

Volatile output at individual arcs – SO$_2$ and the power law distribution
In this section, we provide estimates of the ^{3}He (and other volatile) fluxes from individual arc segments worldwide. To achieve this objective, we use time-averaged SO_2 flux measurements from 43 passively degassing arc volcanoes (Andres and Kasgnoc, 1998) coupled with our own compilation of approximately 700 volcanic and hydrothermal gas

compositions. It must be borne in mind that the accuracy of individual COSPEC measurements can vary from 10-40% (Stoiber et al., 1983) and this error will propagate through to the final estimates. The time-averaged volcanic SO_2 emission rates were compiled from approximately 20,000 individual measurements dating from the early 1970's to 1997 (Andres and Kasgnoc, 1998). Based on this extensive data set, Andres and Kasgnoc (1998) found that SO_2 emissions during eruptions contributed only 1% to the total volcanic SO_2 flux. This conclusion supports earlier work of Berresheim and Jaeschke (1983) who showed that 90% of the SO_2 is emitted during non-eruptive events. Although there are reports of high SO_2 flux rates during eruptive periods (e.g. ref), the eruptions are short-lived and extrapolation of the flux rates to longer time intervals probably questionable. Therefore, in our treatment of SO_2 fluxes in this section, we feel justified in using fluxes which were derived for passively degassing volcanoes only. Furthermore, we recognize that it is impossible to measure the emissions from every single volcano; therefore, this necessitates adoption of an extrapolation procedure to account for the (small) SO_2 flux that is not measured directly. We have followed the methodology of Brantley and Koepenick (1995) who found that if the distribution of volcanic emissions follows a power law, there is an empirical relationship between the cumulative number of volcanoes (N) having or exceeding a given emission rate (f) and the emission rate itself. The relationship takes the form:

$$N = a \, f^{-c} \tag{1}$$

where N is the number of volcanoes having an emission rate $\geq f$ and a and c are constants. If the constant $c < 1$, the total volcanic flux (f_{tot}) can be calculated using the following approximation:

$$f_{tot} = f_1 + f_2 + f_3 + \ldots f_N \, [\, (c/\{1-c\})* (N+1)* (N/\{N+1\})^{1/c}] \tag{2}$$

where N refers to the Nth largest flux. Brantley and Koepenick (1995) found that the global emission of SO_2 is governed by a power law distribution (c = 0.8) so that an estimate of the total SO_2 flux can be made using a relatively small number of volcanoes. They cautioned, however, that only larger volcanoes (log f $\geq$ 8.5) followed a power law distribution.

In spite of this caveat, we have attempted to use the power law distribution to estimate the SO_2 fluxes for individual arcs worldwide. Andres and Kasgnoc (1998) have tabulated the SO_2 flux for 49 volcanoes representing 11 distinct arc systems, and we have used these estimates to derive the total fluxes for each of these arcs. We adopt two different approaches:
- We have assumed that the global value of c (= 0.8; Brantley and Koepenick, 1995) is applicable to each individual arc segment. Therefore, we can calculate f_{tot} from equation 2 above and the tabulated fluxes for volcanoes from each arc.
- We calculate a different c-value for use with each individual arc segment. In the case of Central America, for example, we plot log (N) versus log (f_{SO2}) for 11 volcanoes, and assuming a linear correlation (power law distribution), derive c

from the gradient (Fig. 4). This value of c is used in equation 2 to derive the total flux for that arc.

In Table 7, we show the results for 11 arc segments using these two approaches. Summing the individual arc fluxes, we obtain SO_2 flux estimates (in mol/yr) of 2.80 x 10^{11} (c= 0.8) and 2.62 x 10^{11} (various c-values). Both values compare well with previous estimates using variants of the same (power law) approach - 2-3 x 10^{11} mol/yr (Brantley and Koepenick, 1995); 2.92 x 10^{11} mol/yr (Stoiber et al., 1987) and 2.4 x 10^{11} mol/yr (Berresheim and Jaeschke, 1983). Although the agreement is encouraging, one point of concern is that there appears a large discrepancy between summing the individual fluxes at some arcs and the total (extrapolated) flux. For example, the sum of the measured fluxes for the Andes lies between 43% and 60% of the total extrapolated flux (depending upon the chosen c-value). For comparison, Andes and Koasgnoc (1998) found that - on a global basis - the 'additional' extrapolated flux amounted to 19% of the total i.e., the sum of the measured fluxes was 81% of the total flux. It is noteworthy that calculating c-values for individual arcs seems to decrease the discrepancy between summed and extrapolated fluxes. Additionally, it seems that the large extrapolation appears to affect mostly arcs with small numbers of volcanic SO_2 fluxes (e.g. Andes, Antilles, New Zealand, Philippines – see Table 7). Therefore, while accepting the flux extrapolations give a useful first-order estimate of the SO_2 flux for individual arcs, we caution that not all individual arc flux estimates can be treated with the same degree of confidence. Clearly, the situation will improve as more SO_2 flux measurements become available.

It is interesting that the highest SO_2 emissions are from volcanic arcs in the Papua New Guinea -SW Pacific region - 8.5 – 10.1 (x 10^{10}) mol/yr. However, we note again that the sum of individual flux is significantly less (35-42%) than the extrapolated values, and that the flux extrapolation is weighted by one large value – from Bagana in the Soloman Islands. At the other extreme, the lowest emissions are from the Alaska-Aleutians arc with a SO_2 flux of only 5.6 x 10^8 mol/yr, or less than 1% of the largest value.

In Table 8 we report a compilation of volcanic gas chemistries for over 700 individual analyses of arc-related volcanic and hydrothermal fluids. In an attempt to obtain a more representative picture of the chemical variability, we present the database as median molar ratios which gives less weight to extreme values. In this compilation, S_t is the total S, i.e. SO_2 + H_2S, and $N_{2,exc}$ is the amount of "excess" N_2 after correction for N_2 contributed from meteoric sources in the volcanic edifice. The "excess" N_2 is calculated using

$$N_{2,exc} = N_{2,\ measured} - (40 \times [Ar]) \qquad\qquad (3)$$

where [Ar] is the measured argon concentration, which is assumed to be derived solely from air-saturated water in equilibrium with the atmosphere (see Fischer et al., 1998). With reference to Table 8, there are two outliers in the CO_2/S_t column - the Philippines arc (104.5) and New Zealand (28.7) - which are both significantly higher than typical 'arc-like' values of ~5 (Giggenbach, 1996). We suggest that the available database in

these two cases may be biased to mainly low-temperature hydrothermal fumaroles and geothermal fluids which would act to preferentially remove sulphur species (Giggenbach, 1996). Therefore, in our calculations of volatile fluxes (below), we assume a value of 5 for the CO_2/S_t ratio of both these arcs.

In Table 9 we couple our estimates of the SO_2 flux at various arcs (Table 7) with our compilation of the gas chemistry (Table 8) to produce an estimate of the fluxes of a number of volatile species (CO_2, N_2, $N_{2,exc}$, ^4He, ^3He and Ar) for 11 arcs worldwide. The largest emitter of volatiles (in an absolute sense) is the arc systems of Papua New Guinea and the South-west Pacific although it must be cautioned that these fluxes are derived using data from the Indonesia arcs – no gas chemistry is yet available for these regions. The northern Pacific arcs (Alaska-Aleutians and Kamchatka-Kuriles) are relatively poor emitters of volatiles, and this presumably reflects the virtual absence of carbonate sediment in this region (see Table 10).

The flux estimates in Table 9 are based on measured SO_2 emissions of 45 individual arc volcanoes from 11 regions. However, a significant number of arcs have only little or no SO_2 flux data – these include South Sandwich, Mexico, Cascadia, Izu-Bonin, Ryuku, Marianas, Makran, Andanan, E-Sunda, Vanuatu and Tonga. This is somewhat surprising as there are a total of 106 historically active volcanoes in these regions (Simkin and Siebert, 1994). If we make a rather crude analogy to Central America, where approximately one-third of the 32 historically-active volcanoes emit measurable SO_2, we would expect ~35 of these 106 volcanoes to contribute to the global SO_2 flux. These 35 volcanoes would be expected to contribute a total of ~0.54×10^{11} mol/yr if the median flux of the measured volcanoes (1.54×10^9 mol/yr) is an appropriate figure for their individual SO_2 fluxes. This figure can be added to the sum of SO_2 fluxes for the 11 measured arcs (2.62×10^{11} mol/yr) to yield an estimate of 3.2×10^{11} mol/yr for the total flux of SO_2 from all arc volcanoes worldwide.

To estimate the global flux of the volatiles other than SO_2 we need to make the assumption that the additional SO_2 added (~20%) scales proportionally to the other volatile species. In effect, the volatile ratios (e.g. CO_2/S_t etc) of the unmeasured volcanoes must equal the average values of the 11 arcs where data is available. Under this assumption, global estimates of various volatile fluxes are given in the last row of Table 9.

With respect to helium (Table 7), we note that the total global arc flux is 1.2×10^7 mol/yr which gives a total ^3He flux of approximately 92 mol/yr - for a mean arc $^3He/^4He$ ratio of $5.4 R_A$ (from Table 1). This estimate of the ^3He flux from arcs falls within a factor of 2 of that by Torgersen (1989) but agrees within error with two other estimates - Allard (1992) estimated 70 mol/yr and Marty and LeCloarec (1992) 75 mol/yr (Table 6). This consistency bodes well for our approach of assuming a power law distribution to volatile fluxes at individual arcs, and for our admittedly crude method of estimating fluxes from non-represented arcs. Similarly, our estimate for the total arc flux of CO_2 (1.6×10^{12} mol/yr) shows remarkable agreement with other published values (Table 6). As we

discuss in the next section, our estimate of the global arc N_2 flux is higher than that of Sano et al. (2001) due the availability of a significantly more extensive (and presumably more representative) database of gas chemistries.

Using helium to resolve volatile provenance
Volatile flux estimates derived in the previous section, both for arcs individually as well as arc-related volcanism globally, make no distinction as to the source or provenance of the volatiles. However, in order to assess the chemical mass balance between output at arcs and input associated with the subducting slab, the total arc output flux must be resolved into its component structures. In this way, the fraction of the total output which is derived from the subducted slab can be quantified and compared with estimates of the input parameter. As we show in this section, helium has proven remarkably sensitive in discerning volatile provenance. We use CO_2 and N_2 to illustrate the case.

CO_2 provenance at arcs: The ratio $CO_2/^3He$ is significantly higher in arc-related terrains compared to mid-ocean ridge (MOR) spreading centres. MOR spreading centres have $CO_2/^3He$ ratios $\sim 2 \times 10^9$ (Marty and Jambon, 1987; Marty and Tolstikhin, 1998) whereas island arcs have $CO_2/^3He$ values $\geq 10^{10}$ (Marty et al., 1989; Varekamp et al., 1992; Sano and Marty, 1995; Sano and Williams, 1996; Van Soest et al., 1998). Such high values have been used to argue for addition of slab carbon to the source region of arc volcanism. However, in addition to the slab (sedimentary veneer and underlying oceanic basement), there are other potential contributors to the total carbon output – the mantle wedge and/or the arc crust through which magmas traverse en route to the surface. Distinguishing between these various sources is possible by considering carbon and helium together (both isotopic variations and relative abundances).

In the first instance, a number of workers (Varekamp et al., 1992; Sano and Marty, 1995; Sano and Williams, 1996) approximated the C-output at arcs using a three endmember model consisting of MORB mantle (M), and slab-derived marine carbonate/limestone (L) and (organic) sedimentary components (S). Sano and Marty (1995) used the following mass balance equations:

$$(^{13}C/^{12}C)_o = M(^{13}C/^{12}C)_M + L(^{13}C/^{12}C)_L + S(^{13}C/^{12}C)_S \qquad (3)$$

$$1/(^{12}C/^3He)_o = M/(^{12}C/^3He)_M + L/(^{12}C/^3He)_L + S/(^{12}C/^3He)_S$$
$$(4)$$

$$M+S+L = 1 \qquad (5)$$

where O = observed. It should be noted that application of these equations first involves conversion of carbon isotope ratios (in the δ-notation) to absolute $^{13}C/^{12}C$ values (see Sano and Marty, 1995). Then, it is possible to determine the relative proportions of M-, L- and S-derived carbon in individual samples of arc-related geothermal fluids. Appropriate endmember compositions must be selected, and both Sano and Marty (1995) and Sano and Williams (1996) suggest $\delta^{13}C$ values of -6.5‰, 0‰, and -30‰ (relative to

PDB) with corresponding $CO_2/^3He$ ratios of 1.5 x 10^9; 1 x10^{13}; 1 x 10^{13} for M, L, and S respectively. The estimates derived for M-, L- and S-derived carbon are particularly sensitive to the choice of the mantle $CO_2/^3He$ ratio as well as the sedimentary $\delta^{13}C$ value.

Based on the analysis of arc-related geothermal samples from 30 volcanic centres worldwide and utilizing high, medium and low temperature fumaroles, Sano and Williams (1996) estimated that between 10 and 15% of the arc-wide global CO_2 flux is derived from the mantle wedge - the remaining 85-90% coming from decarbonation reactions involving subducted marine limestone, slab carbonate and pelagic sediment. Subducted marine limestone and slab carbonate supply the bulk of the non-mantle carbon - approximately 70-80% of the total carbon - the remaining ~10-15% is contributed from subducted organic (sedimentary) carbon. With this approach, therefore, it is possible to attempt more realistic volatile mass balances at arcs. It is noteworthy, however, that most studies ignore the arc crust as a potential source of carbon. Although this omission may not be significant in intra-oceanic settings, this is unlikely to be the case at all localities (see discussion regarding the Lesser Antilles – next section).

N₂ provenance at arcs: Using an approach analogous to that for carbon, Sano and co-workers (Sano et al., 1998b; 2001) have recently directed attention at understanding the nitrogen cycle at subduction zones. Again, the problem is to identify and quantify the various contributory sources to the volcanic output: however, a major concern in this case is atmospheric nitrogen. There are three major sources of nitrogen at subduction zones: the mantle (M), atmosphere (A) and subducted sediments (S), and each has a diagnostic $\delta^{15}N$ value and $N_2/^{36}Ar$ ratio. Therefore, observed (O) variations in these two parameters for individual samples can be resolved into their component structures using the following equations (Sano et al., 1998b):

$$(\delta^{15}N)_o = M(\delta^{15}N)_M + L(\delta^{15}N)_A + S(\delta^{15}N)_S \tag{6}$$

$$1/(N_2/^{36}Ar)_o = M/(N_2/^{36}Ar)_M + A/(N_2/^{36}Ar)_A + S/(N_2/^{36}Ar)_S \tag{7}$$

$$M+S+A = 1 \tag{8}$$

Note that the noble gas isotope ^{36}Ar is used in this case since degassing is not expected to fractionate the $N_2/^{36}Ar$ ratio due to the similar solubilities of nitrogen and argon in basaltic magma - this is not the case for helium and nitrogen, and degassing corrections may be necessary if the $N_2/^3He$ ratio is used (Sano et al., 2001). In the above scheme, endmember compositions are generally well constrained: the mantle and sedimentary endmembers both have $N_2/^{36}Ar$ ratios of 6 x 10^6 (air is 1.8 x 10^4) but their $\delta^{15}N$ values are distinct. The upper mantle has a $\delta^{15}N$ value of -5 ± 2 ‰ (Marty and Humbert, 1997; Sano et al., 1998b) whereas sedimentary nitrogen is assumed to be +7 ± 4 ‰ (Bebout, 1995; Peters et al., 1978) (air has $\delta^{15}N$ = 0 ‰). The wide difference in $\delta^{15}N$ between the potential endmembers makes this approach a sensitive tracer of N_2 provenance.

Gas discharges from island arc volcanoes and associated hydrothermal systems have $N_2/^{36}Ar$ ratios which reach a maximum of 9.7 x 10^4, with $\delta^{15}N$ values up to +4.6 ‰ (Sano et al., 2001). This would indicate that a significant proportion (up to 70%) of the N_2 could be derived from a subducted sedimentary or crustal source. The situation is reversed in the case of BABB glasses, which have significantly lower $\delta^{15}N$ values (-2.7 to +1.9 ‰): this implies that up to 70% of the nitrogen could be mantle-derived. A first-order conclusion from this observation is that N_2 is efficiently recycled from the subducting slab to the atmosphere and hydrosphere through arc and back-arc volcanism, with the flux probably weighted towards the arc flux. After correction for the atmospheric contribution, Sano et al. (1998b) estimate the total flux of N_2 through subduction zones (arc and back-arc regions) worldwide at 6 x 10^8 mol/yr (by normalizing to the arc ^3He flux). Interestingly, this value is almost 40-times lower than our estimate of N_{exc} output (2 x 10^{10} mol/yr; Table 9) based on integrating fluxes from different arcs. This results from Sano et al. (2001) adopting a $N_2/^3He$ ratio of 5.6 x 10^6 for arc volcanics based on a relatively small database of 11 geothermal samples. Our database is comprised of >700 geothermal and hydrothermal fluid analyses with a median $N_2/^3He$ ratio of 2.6 x 10^8 – approximately a factor of 40 higher.

Problematic issues regarding estimates of volatile output at arcs
There are two major issues of concern with the approach of using $CO_2/^3He$ and $N_2/^{36}Ar$ (or $N_2/^3He$) ratios in combination with $\delta^{13}C$ and $\delta^{15}N$ values to constrain the sources of volatiles at arcs. The first issue is the selection of endmember isotopic and relative elemental abundances - this factor has a profound effect on the deduced provenance of the volatile of interest. The second is the assumption that various elemental (and isotopic) ratios observed in the volcanic products are representative of the magma source. Both have the potential to compromise the accuracy of the output flux estimates.

In the case of CO_2, the methodology of Sano and co-workers assumes that subducted marine carbonate and sedimentary organic matter can be distinguished as potential input parameters based solely on their perceived C-isotopic compositions prior to subduction (0 ‰ versus -30 ‰ respectively). However, this approach ignores the anticipated evolution of organic-derived CO_2 to higher $\delta^{13}C$ as a function of diagenetic and/or catagenetic changes experienced during subduction (Ohmoto, 1986). In the southern Lesser Antilles, for example, Van Soest et al. (1998) calculated that >50% of the total carbon would be assigned to an organic, sedimentary origin if an endmember S-value of - 10 ‰ were chosen - as opposed to <20 % for an adopted endmember value of -30 ‰. In this scenario, it was suggested that the large sedimentary input implied by adopting a heavier $\delta^{13}C$ sedimentary endmember could be accommodated by loss of CO_2 from the arc crust which is particularly thick in this portion of the arc. This example illustrates the point that a realistic mass balance at arcs is impossible without taking into account (a) the effect of subduction on the evolution of the C-isotopic signature of the sedimentary input, and (b) the possibility of an additional input from the arc crust. Note, however, that not all arcs require a crustal input of volatiles. For example, Fischer et al. (1998) showed that the volatiles discharged from the Kurile Islands arc (75 tons/day per volcano) could be supplied from subducted oceanic crust and mantle wedge alone.

The second potential complication is the possible fractionation of CO_2, N_2, and He during subduction and/or subsequent magma degassing. Little has been reported on elemental fractionation during the subduction process but recent studies at Loihi Seamount have shown that magma degassing can exert a strong control on resultant $CO_2/^3He$ ratios as sampled in hydrothermal fluid discharges. Hilton et al. (1998) reported large variations in $CO_2/^3He$ ratios at Loihi Seamount which were correlated with the composition of the magma undergoing degassing. For example, as helium is more soluble in tholeiitic basalt than CO_2 (i.e., $S_{He}/S_{CO2} > 1$ where S = solubility), the $CO_2/^3He$ ratio in the melt phase will evolve to lower values as a function of fractionation style (Rayleigh or Batch) and extent of degassing. Measured $CO_2/^3He$ ratios in fluids during periods of tholeiitic volcanism were low (~ 5 x 10^8). In contrast, $CO_2/^3He$ ratios ~ 10^{10} were recorded in other active periods, which is consistent with degassing of alkalic magmas (in this case - $S_{He}/S_{CO2} < 1$). In order to obtain a meaningful estimate of the carbon budget in arcs, therefore, the initial (pre-degassing) $CO_2/^3He$ ratio is of prime importance, and it is often assumed that the measured $CO_2/^3He$ ratio equates to the initial magmatic value – as shown above for Loihi Seamount, this may not necessarily be the case. The same issues of degassing-induced changes to elemental ratios apply also to the N_2-He-Ar systematics used to resolve the provenance of nitrogen in arcs (Sano et al., 2001).

A related concern is that of isotopic fractionation of carbon (or nitrogen) during subduction and/or magma degassing. Sano and Marty (1995) have concluded that arc-related high-temperature fluids are likely to preserve the $\delta^{13}C$ values of the (magmatic) source based on comparisons of $\delta^{13}C$ values in fluids and phenocrysts. Furthermore, they cite evidence of overlapping $\delta^{13}C$ values between high- and medium-to-low-enthalpy hydrothermal fluids, leading to the general conclusion that any fractionation induced by degassing and/or interactions within the hydrothermal system must be minimal. On the other hand, Snyder et al. (2001) have argued that geothermal fluids in Central America have experienced 1-2 ‰ shifts in $\delta^{13}C$ resulting from removal of bicarbonate during slab dewatering and/or by precipitation of calcite in the hydrothermal system. It should be noted, however, that even if observed values of $\delta^{13}C$ in arc-fluids are fractionated, the magnitude of the isotopic shifts proposed by Snyder et al. (2001) will make an minor difference only to calculations involving the source of carbon. To date, there is no evidence of nitrogen isotopic fractionation during magmatic degassing (Marty and Humbert, 1997).

Volatile output at the back-arc and fore-arc regions
In addition to supplying volatiles which are lost via arc-related volcanism, the subducting slab may also contribute volatiles to both the back-arc and fore-arc regions. To complete a realistic mass balance for subduction zones, therefore, it is essential to quantify volatile fluxes at the back-arc and fore-arc. As we discuss below, both fluxes are severely under-constrained at present.

Volatile data, encompassing both major volatile phases (CO_2, N_2) and noble gases (He and Ar) are available for a number of back-arc basins including the North Fiji Basin,

Mariana Trough and Manus Basin (Ishibashi et al., 1994; Nishio et al., 1998; Sano et al., 1998a; Marty and Zimmermann, 1999; Sano et al., 2001). A wide range in $CO_2/^3He$ ratios has been reported – from 2.5×10^8 (North Fiji Basin) to 2.2×10^{11} (Manus Basin). There are considerable differences in the treatment of this database. On the one hand, Nishio et al. (1998) reporting data for the North Fiji Basin argue that the value of the mantle $CO_2/^3He$ ratio in this region is 2×10^8: in this way, they calculate that samples with higher $CO_2/^3He$ ratios (up to 9.2×10^9) contain up to 90% slab-derived carbon. On the other hand, Sano et al. (1998a) recognize that measured $CO_2/^3He$ ratios in the Mariana Trough could be fractionated during degassing. After taking account of changes in the ratio due to degassing, the measured $CO_2/^3He$ ratios correct to a value close to that of MORB ($\sim 2 \times 10^9$) implying that the carbon is wholly of mantle derivation. The different interpretations have profound effects on the estimate output flux from back-arc basins. If we scale the mid-ocean ridge ^3He flux (1000 mol/yr for $\sim 6 \times 10^4$ km of ridges) to the length of back-arc ridges ($\sim 2.4 \times 10^4$ km; Uyeda and Kanamori, 1979) and use the extreme $CO_2/^3He$ ratio of the North Fiji Basin (9.2×10^9) as representative of a back-arc basin source region (with a slab contribution), then the CO_2 flux from back-arc basins (globally) is 3.7×10^{12} mol/yr – of which up to 90% (3.3×10^{12} mol/yr) could be derived from the slab. This estimate would make the back-arc CO_2 flux comparable with that for MOR ($2.2 \pm 0.9 \times 10^{12}$ mol/yr; Marty and Tolstikhin, 1998), and significantly higher than most estimates for arc volcanism (Table 6). Alternatively, if we accept the arguments of Sano et al. (1998a), the output of slab-derived CO_2 via back-arc volcanism is essentially zero.

The same uncertainty in back-arc flux rates applies also to N_2. Limited data on BABB glasses from the Mariana Trough, the Manus and North Fiji Basin show $N_2/^3He$ ratios ranging from 1.16×10^6 to 1.37×10^7 and $\delta^{15}N$ values varying between -2.7 and +1.9 ‰ (Sano et al., 2001). Therefore, depending upon the chosen endmember composition, the sediment contribution to the back-arc N_2 flux can vary between zero and close to 40 %. In the latter case, a significant fraction (one-third) of the available slab-derived nitrogen is recycled to the surface via back-arc volcanism as opposed to two-thirds via the arc (Sano et al., 2001).

Although volatile flux estimates from back-arc regions vary greatly, the situation is even more poorly constrained for fore-arc regions. We are unaware of any flux estimates for either major volatiles or noble gases. This is in spite of abundant circumstantial evidence for fluid venting in fore-arc regions e.g. serpentinite diapirism in the Marianas (Fryer et al., 1985) and mud volcanism at various accretionary prisms worldwide (Brown, 1990). Indeed, there are reports of $^3He/^4He$ ratios > crustal production rates (~ 0.05 R_A – Andrews, 1985) in fore-arc regions such as the Nankai Trough (1.9 R_A; Kastner et al., 1993), the Cook Inlet of Alaska (0.8 R_A; Poreda et al., 1988) and Kavachi volcano in the Solomon Islands (6.9 R_A; Trull et al., 1990) - this would indicate a direct output of mantle-derived volatiles. However, there are no estimates of the scale of this phenomenon.

The alternative approach to estimating fore-arc losses of volatiles is somewhat circular and based upon mass balance. For example, the estimated carbon load of incoming material at trenches worldwide (sedimentary carbonate, sedimentary organic carbon and oceanic meta-basalts) is 1.2, 0.8, and 3.4 ($x10^{12}$ mol/yr) respectively (Bebout, 1995; Alt and Teagle, 1999; Plank and Langmuir, 1998). This total (5.4 $x10^{12}$ mol/yr) far exceeds that of the carbon released via arc magmatism (~3 $x10^{12}$ mol/yr; Table 6), implying that a substantial amount of carbon is either released at the fore-arc or by-passes the zone of magma generation and is recycled into the mantle. Whereas there is considerable leeway in all these estimates, the uncertainty is compounded by debate on whether the zone of magma generation acts as a barrier to further subduction of volatiles (Staudacher and Allegre, 1988) or if various C-bearing phases are stable at the likely P-T conditions below the arc so that deep(er) subduction can occur (cf. Kerrick and Connolly, 2001). In this latter scenario, if the input of carbon to the mantle via subduction matches output via MOR (i.e. steady-state upper mantle and no losses to the back-arc) then approximately 2 x 10^{12} mol/yr (the MOR output; Marty and Tolstikhin, 1998) by-passes the zone of magma generation leaving a residual 0.4 x 10^{12} mol/yr potentially available for loss via the fore-arc. There is considerable latitude in these figures (and assumptions inherent in the approach): for these reasons, therefore, we caution that constraining volatile losses at the fore-arc by this mass balance approach be treated with scepticism.

The volatile input via the trench

In this section, we provide estimates of the volatile flux input– of both noble gases (He, and Ar) and major volatiles (CO_2, N_2 – and H_2O) - via the trench. We consider both the subducted sediment load as well as the underlying crustal basement (of thickness 7 km). Note that the volatile input parameter can be calculated for an extensive listing of subduction zones: however, the output parameter via arcs (Table 9) is well constrained by flux data for a limited number of arcs only. For these arcs, at least, we have a direct comparison between input and output for specific volatile species. However, by extrapolating the (limited) output data to arcs worldwide, we can address the question of volatile recycling between the mantle and crust, hydrosphere and atmosphere from a global perspective

In Table 10, we compute the volatile fluxes into the subduction zone for individual arcs using (a) available noble gas, H_2O, CO_2 and N_2 concentration data for oceanic sediments and oceanic (crustal) basement, and (b) estimates of sediment and crust fluxes at each arc segment. In this compilation, it is important to note that the fluxes refer to volatiles potentially entering the subduction zone at the site of the trench – the effects of sediment off-scraping and/or underplating (Von Huene and Scholl, 1991) on the volatile fluxes are not considered. The following points are relevant in the computation of the volatile flux data (Table 10):

- There is limited noble gas data available for oceanic crust. However, Staudacher and Allegre (1988) report He and Ar data for 2 fine-grained basalt samples from the Indian Ocean. We note that although we adopt these data, the samples are of Jurassic age (~108 Myr) so their noble gas contents may not necessarily be appropriate for all types of subducting oceanic crust. Similarly, there is limited noble gas data available for sedimentary material, and we again use

concentrations from Staudacher and Allegre (1988) obtained for sediments from the South West Indian Ridge. With the exception of helium, noble gas contents of oceanic sediments are generally higher than oceanic basalts.

- There are 3 separate values for the water content of the subducting slab. The sediment H_2O contents are given on an arc-to-arc basis by Plank and Languir (1998) and represent bound (not porewater) contents of various drill-core lithologies proximal to the arc in question. A value of 3.4 wt.% is used for water bound in oceanic crust assuming a 50:50 mix of basalt and gabbro (Schmidt and Poli, 1998). Finally, a value of 1.2 wt.% H_2O and termed 'available water', is considered 'available' for the generation of arc mamas following water loss from dehydration and diagenetic processes associated with the early stages of subduction (Schmidt and Poli, 1998).
- In an analogous fashion to water, the CO_2 concentrations in sediments come from an arc-by-arc compilation of carbonate contents of various drill core lithologies (Plank and Langmuir, 1998). The amount of reduced (organic) carbon in sediments is taken as 1% based on average contents of metamorphosed sediments of the Catalina Schist (Bebout, 1995). A value of 0.214 wt.% is used for the amount of CO_2 stored in altered oceanic crust (Alt and Teagle, 1999).
- The N_2 concentrations are average values of oceanic sediments (0.01 wt.%) and crust (0.001 wt.%) - from Bebout (1995).

In their compilation of the characteristics of oceanic sediments, Plank and Langmuir (1998) has shown that both the amount and chemical composition of sediments being subducted are highly variable: we emphasise that the same observation is true also for the major volatile components, H_2O and CO_2. However, due to the paucity of data, it is currently not possible to evaluate if there is any regional variability in the noble gas contents of oceanic sediments and their crystalline basements.

The input fluxes of various volatile species (Table 10) can now be compared to various output fluxes through arc volcanism (Table 9) to assess the extent of volatile mass balance. At this stage, we ignore possible volatile losses at the back-arc given the large uncertainty in actual values. Also note that in the case of subducted carbon, it is important to distinguish between reduced sedimentary carbon, sedimentary carbonate and carbonate of the altered oceanic crust.

Volatile mass balance at subduction zones
Before comparing the output to input fluxes for the various volatile species, it is necessary first to resolve the carbon output via the arc into its components parts reflecting carbon provenance from the mantle wedge, and slab-derived carbonates and organic carbon. In Table 11, we report % contributions to the CO_2 output using the mass balance equations of Sano and Marty (1995) but adopting a $\delta^{13}C$ value for the sedimentary endmember (S) of −20‰. Bebout (1995) shows convincing evidence of a progressive increase in $\delta^{13}C$ of carbonaceous material with increasing metamorphic grade in the Catalina Schist, and Van Soest et al. (1998) discuss the effect of adopting a higher $\delta^{13}C$ value for the S-endmember on the calculation of CO_2 provenance. Resolution of the CO_2 output into M-, L- and S- components is shown in Fig. 5 for arcs where sufficient data is

available. In each case, we report the median values for M, L and S. The limestone-derived component dominates at all localities.

In Tables 12 (major volatiles) and 13 (He and Ar) we compute ratios of the output to input fluxes for the various individual arcs. The output fluxes are given in Table 9 – modified in the case of carbon for provenance (L, S, and M; see Table 11). The input fluxes are given in Table 10. It is noteworthy that the ratios of output/input vary significantly between individual arcs. We point out the following features of interest with reference to Tables 12 and 13.

- The sedimentary output of CO_2 (S) significantly exceeds the input of organic sedimentary carbon for 4 of the 9 arcs where data are available (Andes, Japan, New Zealand and the Philippines). For these localities, an additional source of organic carbon is required: the uppermost arc crust seems the only likely possibility. At the other arcs, the input of organic carbon exceeds the output via the arc, and suggests that either sediment accretion and/or off-scraping of subducting sediments could be prohibiting the transport of organic carbon to the zones of magma generation. For Central America the ratio is very close to unity suggesting that the output from the arc is nearly balanced by the input of organic sedimentary carbon.

- The output of carbonate-derived CO_2 (L), cannot be balanced with the amount of sedimentary carbonate CO_2 being subducted except for the Central American and Sunda (Indonesia) volcanic arcs. This would suggest that, in both these localities, sediment-derived carbonate may be efficiently transported to the zones of magma generation. When carbonate CO_2 from the subducting altered oceanic crust is taken into account, the output can be supplied solely from the slab: indeed, at all localities, except Japan, only a fraction of the input CO_2 is necessary to supply the output. These figures reinforce the notion that subduction zones act as conduits for the transfer of carbon into the mantle (Kerrick and Connolly, 2001).

- In general, the amount of excess (non-atmospheric) N_2 being emitted from arc volcanoes is less than the amount of N_2 being subducted (with the exception of the Andes and Japan). This would imply that either that a significant amount of subducted N_2 may not reach the zones of arc magma generation and/or it is retained and lost to the (deeper) mantle. The observation of large increases in the C/N ratio of Catalina Schists as a function of increasing metamorphic grade (Bebout, 1995) – interpreted as enhanced devolatilisation (loss) of N_2 – would seem to favour the former possibility.

- The flux of H_2O from each arc segment greatly exceeds the amount of water available at the zone of arc magma generation (1.2 wt.% - Schmidt and Poli, 1998). Even when the total amount of water potentially subducted is taken into account (IN total – Table 12), for the most part (excepting Alaska-Aleutians, Indonesia and Kamchatka-Kuriles), output via the arc exceeds input via the trench. Water from the mantle wedge and/or the arc crust must contribute to the output in these cases. Alternatively, the 'excess' water may be meteoric in origin although it must first become incorporated by magma (and contribute to the high 'magmatic' H_2O/CO_2 ratio of 50).

- The ^{3}He output flux exceeds the input parameter in all cases. This is true even in cases (Alaska-Aleutians, Indonesia and Kamchatka-Kuriles) where the potential input of ^{4}He exceeds the output via the arc. The observation that at each locality the ^{3}He/^{4}He ratio of the output flux approaches the MORB value indicates that little, if any, of the slab-derived helium reaches the zones of magma generation.

- A similar pattern is observed for ^{36}Ar – output via the arc greatly exceeds potential input via the trench. The output volatile flux appears dominated by atmosphere-derived ^{36}Ar (thereby validating its use to calculate 'excess' N_2). Likewise, output of ^{40}Ar far exceeds potential input. In the case that all the ^{36}Ar is atmospheric, the excess ^{40}Ar (to raise the average arc ^{40}Ar/^{36}Ar value to 401 – Table 4) can be either crustal (Kennedy et al., 1991) or mantle (Patterson et al., 1994) in origin.

Global implications of volatile recycling at subduction zones

In this final section, we extend our considerations of subduction zone processing of volatiles (input versus output fluxes – previous section) to address the issue of long-term volatile exchange between the surface of Earth and the mantle. We follow the approach of Marty and Dauphas (2002) by relating the ratio of the volatile flux through arc volcanism and the amount of volatiles carried by subducting plates (F_{arc}/F_{sub}) to the Mean Degassing Duration (MDD) of a particular volatile species. The MDD (in years) is the ratio of the total surface inventory of a volatile element (ocean+crust+atmosphere) to the present-day mantle flux, approximated by the MOR flux (assuming that plume degassing is minor compared to ridges). As discussed in general terms in the previous section, a F_{arc}/F_{sub} ratio close to unity implies little or no recycling of subducted volatiles into the mantle beyond the zone of magma generation, a ratio of <<1 implies possible (deep) recycling, and a ratio of >>1 implies that additional contributions to the volatile flux (other than from subducting sediments and oceanic crust) are required. A MDD value less than the age of Earth implies rapid recycling of volatiles between the mantle and surface reservoirs. A MDD value greater than 4.55 Gyr suggests either a decreasing degassing rate with time or the occurrence of a volatile component at the Earth's surface not derived from the mantle, or both. Global averages of F_{arc}/F_{sub} ratios together with MDD values are given in Table 14 and plotted against each other in Figure 6.

In Figure 6, we observe a generally positive correlation between F_{arc}/F_{sub} and MDD indicative of decreasing efficiency in atmosphere-mantle exchange in the order SO_2, CO_2, H_2O, ^{3}He $\approx$ ^{4}He $\approx$ ^{40}Ar, N_2 (ex), ^{36}Ar. Sulphur has a F_{arc}/F_{sub} ratio << 1 and MDD value of << 4.5 Gyr, implying that subduction leads to a rapid and efficient exchange between the atmosphere and mantle. Carbon also has a F_{arc}/F_{sub} ratio < 1 and a MDD value of < 4.5 Gyr - again consistent with efficient recycling between the mantle and atmosphere. Water has a F_{arc}/F_{sub} ratio > 1 and an MDD value greater than the age of Earth. In terms of arc magmatism, this implies that an additional source of water is required other than the amount released from the subducting slab. This additional H_2O may be of surficial (meteoric) or crustal origin.   The MDD value greater than the age of the Earth would be consistent with the notion that the recycling of H_2O into the deeper mantle is less efficient than for CO_2 i.e. only a small proportion of the subducted water bypasses the zone of arc

magma generation to the deeper mantle for later re-emergence at MOR. Helium-4 has a F_{arc}/F_{sub} ratio similar to H_2O and a MDD value also greater than the age of the Earth implying an additional source of He in arcs - most likely from the mantle wedge. This is even more pronounced for [3]He and [40]Ar, which have the highest F_{arc}/F_{sub} ratios, consistent with the idea that He and Ar are not subducted – either to the deeper mantle nor to the zone of magma generation at arcs. Nitrogen and [36]Ar lie off the trend described by SO_2, CO_2, H_2O, He, and [40]Ar in Fig. 6. Nitrogen has a similar F_{arc}/F_{sub} ratio as CO_2 (<1), indicating that N_2 is either partially recycled into the mantle or released in the fore-arc. The large MDD value suggests that recycling into the deep mantle is not very efficient and/or that the mantle degassing rate for N_2 has probably decreased over time. This is consistent with the model of Tolstikhin and Marty (1998) which suggests a vigorous N_2 degassing of the upper mantle early after accretion and possible addition of N_2 from late impacting bodies (e.g. comets). Argon-36 has a F_{arc}/F_{sub} ratio > 1 and the greatest MDD value of all volatiles shown. This implies that Ar is not recycled into the deep mantle, and that the amount discharging from arc volcanoes is mostly of shallow crustal or atmospheric origin.

In terms of the isotopic composition of volatiles in different Earth reservoirs, efficient recycling between the surface and mantle would tend to minimise isotopic differences between reservoirs. This is the case for sulphur and carbon where isotopic differences between the mantle and surface reservoirs are at the level of < 10 ‰. Isotopic differences for water between the mantle and surface (e.g. ocean water) are larger (~70-100 ‰; Poreda et al., 1986): however, there is a huge difference in [40]Ar/[36]Ar ratios between the (upper) mantle (>40,000) and the atmosphere (296). This is consistent with very inefficient recycling of [36]Ar into the deeper mantle, and supports the notion of a subduction barrier for argon (Staudacher and Allegre, 1988). The case of nitrogen is more enigmatic as both the uppermost region of the mantle, supplying mid-ocean ridges, and the mantle source of diamonds seem to be characterized by the same nitrogen isotopic composition (δ^{15}N about – 5 ‰). Because some of the diamonds might have been stored in the sub-continental lithosphere for time periods of 1 Gyr or more (e.g. Richardson et al., 1984), the homogeneity of the mantle sampled by MORB and diamonds suggests little or no contribution of recycled nitrogen which is likely to be heavy (^{15}N-rich) – certainly over the last few Gyr. The initial δ^{15}N value of mantle nitrogen could have been much lighter than presently seen in mantle-derived rock – as low as –30‰ if one assumes an enstatite chondrite composition (Javoy et al., 1986); therefore, the –5‰ composition of MORB and diamonds could be the result of recycling of heavy nitrogen from the surface. In this case, nitrogen recycling would have proceeded early in Earth history. The recent observation by Dauphas and Marty (1999) of heavy nitrogen in rocks and minerals from the Kola magmatic province (Russia), in samples characterized by plume-like helium and neon (Marty et al., 1998), raises the interesting possibility that recycled volatiles are stored in the deep mantle source of plumes. The timescale for residence time of recycled radiogenic tracers in the mantle is of the order of 1 Gyr or more (Hofmann, 1997), suggesting by analogy that recycling of nitrogen in the deep mantle took place essentially in the Proterozoic. If correct, this possibility has far reaching implications for the geodynamics of the mantle, particularly the issue of the duration of plate tectonics. More

volatile data on plume-like material is clearly needed to provide a complementary viewpoint to that given by subduction zone volatiles.

SUMMARY AND FUTURE WORK

This review has focussed on the noble gas systematics of subduction zones. Although a considerable database has been accumulated on the noble gas (and major volatile) characteristics of both arc and back-arc regions, and these are summarised above, there are numerous topics which warrant further and more detailed attention. We suggest that the following list contains realistic objectives where advances can be made:

- Although the helium database is significant for arcs and back-arcs, the same cannot be said for neon and argon – much less so for krypton and xenon. This is due to a combination of obtaining suitable samples (not overwhelmed by air contamination) and analytical limitations. We envisage that future refinements and developments in sample processing (e.g. laser ablation) and/or measurement capabilities will lead to improved and more complete noble gas datasets - which ideally will have complementary major volatile data.

- It is encouraging that techniques are being developed to treat and test noble gas datasets for processes such as magmatic degassing and/or crustal assimilation which may disturb both isotopic and abundance characteristics of magmatic systems. In the case of oceanic basalts, for example, Marty and Zimmermann (1999) and Burnard (2001) provide approaches to recognize and correct for such extraneous effects. In a sub-aerial environment, Hilton et al. (1995) considers crustal contamination of phenocrysts whereas Goff et al. (2000) consider the effects of magmatic degassing on the chemistry of fumarolic gases. More consideration should be given to this topic for all types of samples and localities.

- There remain large uncertainties in estimating volatile fluxes – both for arcs individually as well as for arcs globally. Although progress has been made in the determination of SO_2 (and CO_2) fluxes for a number of arcs, the fluxes of related volatiles (H_2O, N_2 and the noble gases) is not as well known as a result of sparse datasets (particularly for the noble gases other than helium). Additional measurements using both ground- and satellite-based remote sensing techniques have the potential to improve the current database of the magnitude and speciation of volcanic emissions. These techniques need to be applied to both passively degassing volcanoes as well as those actively erupting. Moreover, monitoring studies of single volcanoes are needed to better evaluate flux and compositional variations over long time periods (e.g., see studies of Galeras Volcano, Colombia (Zapata et al., 1997; Fischer et al., 1997) and Vulcano, Italy (Nuccio et al., 1999)). Surprisingly, there are a significant number of arcs with virtually no volatile emission or gas compositional data. A high priority of future work should be the study of these arcs to provide a complementary dataset to well-studied arcs such as Central America.

- The volatile output and composition at fore-arcs and back arcs remains poorly constrained. Currently, we are unaware of any representative volatile flux measurements for fore-arcs. These measurements are critical to arrive at an accurate volatile mass balance of subduction zones, and to evaluate if volatiles are transferred beyond this region to the zone of magma generation and/or to the deeper mantle.

- Better constraints are required for the input parameters (particularly for the noble gases and nitrogen). Additional information on the volatile composition of both oceanic sediments and crustal basement is needed to improve estimates of mass balance at subduction zones.

- More data are required on possible elemental (and isotopic) fractionation of the major and noble gases particularly during both metamorphic devolatilization reactions but also during magma storage, crystallization and degassing. This will provide more realistic endmember compositions to be assigned to slab- and mantle-derived fluids in modelling studies. Progress in this area may come from experimental work on vapour-melt partitioning of volatiles allied with improved datasets on different arc systems with contrasting forcing functions (angle of slab dip, rate of subduction, etc.).

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Table 1. Summary of helium isotope variations in arc-related volcanics and geothermal fluids worldwide

Location (arc segment)	R/R$_A$ (max)	R/R$_A$ (min)	R/R$_A$* (mean) (± 1 S.D.)	N[$]	Crustal thickness[1] (km) + type[4]	Conv. Rate[2] (mm/yr)	Sediment Subducted[3] (km^3/Ma)	Slab Age (Ma)[4]	Refs[5]
N. Lesser Antilles (Saba – Dominica)	8.60	3.31	6.80 ± 1.33	73	30-35 O	20	19a	68	[1-4]
S. Lesser Antilles (Martinique – Grenada)	8.90	1.53	4.93 ± 1.85	82	30-35 O	20	19a	68	[2-4]
Andes – Central Chile	6.84	0.18	3.90 ± 1.74	18	40 C	70	74a	48	[5]
Andes – Northern Chile	6.02	0.82	2.39 ± 1.43	12	70 C	80	29b	82	[5]
Andes - Peru	-	-	2.8	1	70 C			45	[6]
Andes - Equador	4.80	2.10	3.22 ± 0.98	5	66 C			32	[7]
Andes - Columbia	8.84	0.90	5.66 ± 2.41	45	66 C			15 ± 10	[6, 8-10]
Central America	7.93	2.13	5.97 ± 1.44	31	42 C	65	23b	23 ± 5	[11-14]
Mexico	7.34	5.10	6.82 ± 0.97	5	30 C	70	35a	14 - 15	[11, 15]
Cascades	8.19	1.25	6.07 ± 1.93	19	25-35 C	35	34a	8	[11, 16-17]
Alaska	7.89	6.03	7.06 ± 0.75	8	36 C	70	177a	46	[11]
Aleutian Islands	8.01	1.60	5.74 ± 1.54	23	18-25 O	70	177a	54	[11]
Kamchatka	6.33	4.88	5.76 ± 0.54	7	25-45 C	90		90 ± 15	[11, 18]
Kurile Islands	6.76	5.70	6.33 ± 0.43	7	15-30 C	90	48b	119	[11, 19]
NE Japan	8.40	1.70	5.10 ± 1.68	129	27-36 C	105	29a	130	[11, 20-27]
SW Japan (Nankai)*	7.13	3.98	5.61 ± 1.07	16	25 C	30	18a	21	[6, 20, 28]
Taiwan (Ryukyu)	6.15	4.35	5.06 ± 0.65	6	35 C	60	19b	49	[11]
Mariana Islands	7.65	5.30	7.04 ± 0.88	6	15-18 O	90	52b	155	[11, 16]
Philippines	7.60	6.90	7.34 ± 0.24	10	-T	90	33b	-	[11, 29]
Indonesia – East Sunda/Banda arcs	4.50	0.01	2.18 ± 1.23	28	<15 O	70-80			[11, 30-31]
Indonesia - Sumatra	8.80	2.08	6.15 ± 1.74	20	- C	50	96a	55	[32-33]
Indonesia – Java-Flores	8.80	4.50	6.69 ± 1.03	26	25-30 T	75	37a	138	[7, 30, 32-35]
New Zealand (Taupo Volcanic Zone)	8.23	1.45	5.99 ± 1.38	145	36 C	70	24b	98	[36-43]
Tabar (New Ireland arc)	7.54	2.03	6.18 ± 1.37	53					[44]
Italy (Aeolian arc)*	8.00	1.23	5.32 ± 1.03	103	20	9			[20, 45-50]
Italy (Campanian Magmatic Provence)	4.62	0.76	2.52 ± 0.63	52		9			[45-46, 51-53]
GRAND TOTAL	8.90	0.01	5.37 ± 1.87	922					[1-53]

<u>Footnote to Table 1</u>

*   Includes only air- or ASW-corrected ^{3}He/^{4}He data except where no He/Ne ratios are given (see Appendix in Hilton, 1996 for details of the correction procedure).

\$ N = number of individual results incorporated into mean. In the case of duplicate analysis, the higher number is selected. Includes time-series results from single locality.

**   Includes Mt. Etna on Sicily (see Schiano et al., 2001).

*** Xenolith samples from NE Kyushu in SW Japan (Sumino et al., 2000; Ikeda et al., 2001) with 'hotspot' ^{3}He/^{4}He ratios ($>>8R_A$) are not obviously arc-related and are not included in this compilation.

1.   Crustal thickness (in km) from Gill (1981)

2.   Orthogonal convergence rate from Von Huene and Scholl (1991)

3.   Estimated (solid) fraction subducted (x 1000 km^3/Myr) from Von Huene and Scholl (1991) a = Type 1 (accretionary prism forms); b = Type 2 (no net accretion) – from Von Huene and Scholl (1991).

4.   Age of slab (Myr) and type of crust from Jarrad (1986). Types: O = oceanic; C = continental; T = transitional.

5.   Helium isotope data sources: 1= Chiodini et al. (1996); 2 = van Soest et al. (1998); 3 = Pedroni et al. (1999); 4 = van Soest et al. (2002); 5 = Hilton et al. (1993); 6 = Sano and Marty (1995); 7 = Fischer and Sano (unpubl.); 8 = Williams et al. (1987); 9 = Sano et al., (1997); 10 = Lewicki et al. (2000); 11 = Poreda and Craig (1989); 12 = Hilton, Goff and McMurtry (unpubl.); 13 = Janik et al. (1992); 14 = Sano and Williams (1996); 15 = Taran et al. (1998); 16 = Craig et al. (1978); 17 = Dodson and Brandon (1999); 18 = Fischer et al. (1999); 19 = Fischer et al. (1998); 20 = Marty et al. (1989); 21 = Igarashi et al. (1992); 22-26 = Sano et al (1984; 1986; 1988; 1991; 1994); 27 = Porcelli et al. (1992); 28 = Craig and Horibe (1994); 29 = Giggenbach and Poreda (1993); 30 = Hilton and Craig (1989); 31 = Hilton et al. (1992); 32 = Gasparon et al (1994); 33 = Hilton and Fischer (unpubl); 34 = Allard, (1983); 35 = Sano et al. (2001); 36 = Torgersen et al. (1982); 37 = Hulston et al. (1986); 38 = Sano et al. (1987); 39-40 = Hulston and Lupton (1989; 1996); 41 = Marty and Giggenbach (1990); 42 = Giggenbach et al. (1993); 43 = Patterson et al. (1994); 44 = Patterson et al. (1997); 45 = Sano et al. (1989); 46 = Marty et al. (1994); 47 = Tedesco et al. (1995); 48 = Tedesco and Nagao (1996); 49 = Allard et al. (1997); 50 = Nakai et al. (1997); 51 = Tedesco et al. (1990); 52 = Graham et al. (1993); 53 = Tedesco et al. (1998).

Table 2. Summary of neon isotope variations in arc-related lavas and geothermal fluids

Location		maximum	minimum	N	Mean (± 1 s.d.)	Refs.[5]
New Zealand	$^{20}Ne/^{22}Ne$	10.59	9.69	9	10.02 ± 0.25	[1]
	$^{21}Ne/^{22}Ne$	0.0554	0.0284	9	0.0332 ± 0.0085	[1]
Central America	$^{20}Ne/^{22}Ne$	10.10	9.56	11	9.79 ± 0.17	[2]
	$^{21}Ne/^{22}Ne$	0.0298	0.0286	11	0.0292 ± 0.0004	[2]
Lesser Antilles[1]	$^{20}Ne/^{22}Ne$	10.55	9.56	65	9.94 ± 0.17	[3]
	$^{21}Ne/^{22}Ne$	n.d.	n.d.	0		
Italy (Aeolian arc)[2]	$^{20}Ne/^{22}Ne$	10.69	9.41	20	9.91 ± 0.33	[4-5]
	$^{21}Ne/^{22}Ne$	0.0397	0.0290	20	0.0323 ± 0.0033	[4-5]
Italy (Vesuvius)[3]	$^{20}Ne/^{22}Ne$	9.95	8.88	11	9.50 ± 0.33	[6]
	$^{21}Ne/^{22}Ne$	0.0451	0.0243	11	0.0337 ± 0.0067	[6]
Japan[4]	$^{20}Ne/^{22}Ne$	10.36	9.73	38	9.89 ± 0.14	[7]
	$^{21}Ne/^{22}Ne$	0.0306	0.0282	34	0.0292 ± 0.0005	[7]
Summary	**$^{20}Ne/^{22}Ne$**	**10.69**	**8.88**	**154**	**9.89 ± 0.24**	**[1-7]**
Summary	**$^{21}Ne/^{22}Ne$**	**0.0554**	**0.0243**	**85**	**0.0309 ± 0.0043**	**[1-2, 4-7]**

Footnote to Table 2
1. Includes both northern and southern segments
2. Etna and Volcano only
3. Campanian Magmatic Provence
4. Includes data from NE and SW (Nankai) Japan.
5. Neon isotope data sources: 1 = Patterson et al., 1994; 2 = Kennedy et al., 1991; 3 = Pedroni et al., 1999; 4 = Nakai et al., 1997; 5 = Tedesco and Nagao, 1996; 6 = Tedesco et al., 1998; 7 = Nagao et al., 1981.

n.d. = not determined.

Table 3. Summary of argon isotope variations ($^{40}Ar/^{36}Ar$) in arc-related lavas and geothermal fluids

Location	Maximum	minimum	N	Mean (± 1 s.d.)	Refs.[6]
New Zealand	1160	296	22	431 ± 209	[1-3]
Central America	330	290	17	300 ± 9	[4-5]
Lesser Antilles (North)[1]	317	293	21	300 ± 7	[6]
Lesser Antilles (South)[2]	435	286	46	302 ± 21	[6]
Italy (Aeolian arc)[3]	2082	288	116	503 ± 381	[4, 7-10]
Italy (Vesuvius)[4]	301	295	11	298 ± 2	[11]
Japan[5]	325	287	28	304 ± 9	[12]
Summary	**2082**	**286**	**261**	**401 ± 278**	**[1-12]**

Footnote to Table 3
1. Islands from Dominica to Nevis
2. Islands from Grenada to Martinique
3. Etna and Volcano only
4. Campanian Magmatic Province
5. Includes data from NE and SW (Nankai) Japan.
6. Argon isotope data sources: 1 = Torgersen et al., 1982; 2 = Marty and Giggenbach, 1990; 3 = Patterson et al., 1994; 4 = Staudacher and Allegre, 1988; 5 = Kennedy et al., 1991; 6 = Pedroni et al., 1999; 7 = Magro and Pennisi, 1991; 8 = Marty et al., 1994; 9 = Tedesco and Nagao, 1996; 10 = Nakai et al., 1997; 11 = Tedesco et al., 1998; 12 = Nagao et al., 1981.

Table 4. Summary of helium isotope variations in back arc-related volcanics
and hydrothermal fluids.

Location (segment)	R/R$_A$ (max)	R/R$_A$ (min)	R/R$_A$* (mean) (± 1 S.D.)	N$^\$$	Refs[1]
Lau Basin					
Rochambeau Bank	22.1	11.0	16.3 ± 5.3	5	[1-2]
Peggy Ridge	10.9	1.2	8.3 ± 3.1	8	[1-2]
Northern Basin	8.1	5.9	7.2 ± 0.7	9	[2-4]
Central Spreading Center	11.2	7.5	8.6 ± 0.8	14	[2-4]
East Spreading Center	8.9			1	[4]
Valu Fa Ridge	7.8	1.2	5.7 ± 2.6	10	{3, 5]
Total (Lau Basin)	22.1	1.2	8.5 ± 3.8	47	[1-5]
Mariana Trough					
North	8.6	5.7	7.8 ± 0.8	15	[6-7]
Central	8.5	0.85	6.8 ± 2.8	8	[1, 7]]
South	8.8	7.9	8.3 ± 0.3	15	[8]
Total (Mariana Trough)	8.8	0.85	7.8 ± 1.4	38	[1, 6-8]
North Fiji Basin					
N160^o segment	8.8	8.6	8.7 ± 0.1	3	[9]
Triple Junction Area	10.0	7.9	9.1 ± 0.7	16	[9-10]
N15^o segment	9.0			1	[9]
N-S segment	10.3	3.8	8.4 ± 1.5	13	[9-11]
174° E segment	8.8	8.1	8.4 ± 0.9	6	[9]
Total (North Fiji Basin)	10.3	3.8	8.7 ± 1.1	36	[9-11]
Manus Basin					
Seamount	15.2			1	[12]
Extensional Transform Zone	13.5	0.92	10.1 ± 4.3	7	[12]
Manus Spreading Center	12.7	0.67	10.1 ± 4.2	17	[8, 12]
Southern Rifts	8.8	3.4		2	[12]
East Manus Rift	6.4	0.61	3.7 ± 2.4	8	[8, 12-13]
Total (Manus Basin)	15.1	0.61	8.5 ± 4.7	35	[8, 12-13]
Summary	22.1	0.61	8.4 ± 3.2	156	[1-13]

Footnote to Table 4

* Includes only air- or ASW-corrected ^{3}He/^{4}He data except where no He/Ne ratios are given.
$ N = number of individual results incorporated into mean. In the case of duplicate analysis, the higher number is selected.
6. Helium isotope data sources: 1= Poreda (1985); 2 = Poreda and Craig (1992); 3 = Hilton et al. (1993); 4 = Honda et al. (1993); 5 = Bach and Niedermann (1998); 6 = Ikeda et al. (1998); 7 = Sano et al. (1998); 8 = Macpherson et al. (2000); 9 = Nishio et al., (1998); 10 = Ishibashi et al. (1994); 11 = Marty and Zimmermann (1999); 12 = Macpherson et al. (1998); 13 = Marty et al. (2001).

Table 5. Summary of $^{40}Ar/^{36}Ar$ isotope variations in back arc-related volcanics.

Location (segment)	$\frac{^{40}Ar}{^{36}Ar}$ (max)	$\frac{^{40}Ar}{^{36}Ar}$ (min)	$\frac{^{40}Ar}{^{36}Ar}$ (mean) (± 1 S.D.)	N$	Refs[1]
Lau Basin					
Northern Basin	5300	444	2758 ± 2337	7	[1-2]
Central Spreading Center	4900	1206	2429 ± 1140	10	[1-2]
East Spreading Center	461			1	[2]
Valu Fa Ridge	488	293	337 ± 66	11	[1, 3]
Total (Lau Basin)	5300	293	1647 ± 1686	29	[1-3]
Mariana Trough					
North	4480	295	1647 ± 1686	12	[4-5]
Central	4400	338		2	[5]]
South	2734	296	613 ± 636	15	[6]
Total (Mariana Trough)	4480	295	927 ± 1139	29	[4-6]
North Fiji Basin					
N-S segment	3339	532	1512 ± 1583	3	[7]
Total (North Fiji Basin)	3339	532	1512 ± 1583	3	[7]
Manus Basin					
Seamount	1310			1	[8]
Extensional Transform Zone	2680	296	1203 ± 1046	6	[8]
Manus Spreading Center	1764	295	846 ± 563	9	[8]
Southern Rifts	274			1	[8]
East Manus Rift	301	278	293 ± 8	7	[8-9]
Total (Manus Basin)	2680	274	770 ± 701	24	[8-9]
Summary	5300	274	1148 ± 1312	85	[1-9]

Footnote to Table 5

* Includes only air- or ASW-corrected $^3He/^4He$ data except where no He/Ne ratios are given.

\$ N = number of individual results incorporated into mean. In the case of duplicate analysis, the higher number is selected.

7. Helium isotope data sources: 1 = Hilton et al. (1993); 2 = Honda et al. (1993); 3 = Bach and Niedermann (1998); 4 = Ikeda et al. (1998); 5 = Sano et al. (1998); 6 = Hilton et al. (unpublished) 7 = Marty and Zimmermann (1999); 8 = Shaw et al. (unpubl); 9 = Marty et al. (2001).

Table 6. Compilation of volatile fluxes (mol/yr) from arc-related and global subaerial volcanism.

Species	Arc Flux	Reference	Global Subaerial Flux	Reference
^{3}He	200 ± 40	1	275 ± 35	1
	70 ± 25	2	240-310	2
	>75	3	150	3
			3-150	4
	92	5		
^{4}He	2.0 ± 0.13 (x 10^7)	1	3.75 ± 1.35 (x 10^8)	1
	1.23 x 10^7	5		
^{40}Ar	1.9 x 10^8	6		
^{36}Ar	4.7 x 10^5	6		
CO_2	3.1 x 10^{12}	7	0.77 ± 0.58 (x 10^{12})	10
	0.3 ± 0.2 (x10^{12})	4	1.8 x 10^{12}	11
	0.5 ± 0.4 (x10^{12})	10	1.5 x 10^{12}	2
	0.7 x 10^{12}	2	3.3 x 10^{12}	3
	1.5 x 10^{12}	8	2.5 ± 0.5 (x10^{12})	12
	2.5 x 10^{12}	9	1.1 x 10^{12}	13
			5.5 x 10^{12}	9
	1.6 x 10^{12}	14		
N_2	6.4 x 10^8	15	2.8 x 10^9	15
	2.0 x 10^{10}	16		
H_2O	8.0 x 10^{12}	17	55-550 x 10^{12}	13

# Reference	Method
1 Torgersen (1989)	Scaling to MOR ^{3}He flux
2 Allard (1992)	^{3}He/CO_2 ratios plus CO_2 flux
3 Marty and Le Cloarec (1992)	^{210}Po/SO_2 – CO_2/SO_2 and CO_2/^{3}He ratios
4 Marty et al.(1989)	CO_2/^{3}He and CO_2/SO_2 ratios plus SO_2 flux
5 This work (Table 9)	Summation of individual arcs (arc = 5.4R_A)
6 This work (Table 9)	Summation of individual arcs (arc ^{40}Ar/^{36}Ar = 401)
7 Sano and Williams (1996)	C/^{3}He plus ^{3}He flux
8 Varekamp et al. (1992)	C/^{3}He plus mass flux
9 Marty B. and Tolstikhin I. N. (1998)	CO_2/^{3}He ratios plus magma emplacement
10 Williams et al. (1992)	C/S plus S flux
11 Gerlach (1991)	Flux measurement
12 Brantley S. L. and Koepenick K. W. (1995)	Flux measurement
13 LeGuern F. (1982)	Flux measurement
14 This work (Table 9)	Summation of individual arcs
15 Sano et al. (2001)	N/^{3}He plus ^{3}He flux
16 This work (Table 9)	Summation of individual arcs
17 This work	H_2O/CO_2 = 50 and CO_2 flux from ref. 14

Table 7 Summary of SO$_2$ fluxes (x 10^9 mol/yr) – measured and extrapolated using power law distribution

Arc Segment	# volcanoes SO$_2$ flux[1]	Σ measured fluxes	Extrapolated Flux[2]	% measured extrapolated	C-coefficient[3] (r^2-value)	Extrapolated Flux[4]	% measured extrapolated
Andes	3	28.2	65.9	42.8	-0.70 (0.77)	47.3	59.6
Alaska-Aleutians	3	0.41	0.56	73.3	-0.34 (0.84)	(0.34)	-
Antilles	1	1.31	4.41	29.7	-	-	-
Central America	11	20.3	25.1	80.9	-0.46 (0.72)	21.3	95.5
Indonesia	4	1.64	2.76	59.2	-0.55 (0.80)	1.88	86.9
Italy	3	27.2	29.8	91.4	-0.23 (0.92)	27.0	-
Japan	8	20.0	29.6	67.6	-0.60 (0.98)	23.3	85.9
Kamchatka-Kuriles	3	1.64	2.51	65.5	-0.41 (0.92)	1.67	98.2
New Zealand	2	4.67	15.3	30.5	>1	-	-
Papua New Guinea	5	35.8	85.4	42.0	-0.84 (0.92)	100.9	35.5
Philippines	2	5.12	18.2	28.1	-	-	-
GRAND TOTAL	45	146	279.5	52.2		261.8[5]	55.8

1. SO$_2$ flux measurements from Andres and Kasgnoc (1998)
2. Extrapolated flux using methodology of Brantley and Koepenick (1995) assuming imperial constant (c) = global average value of 0.8.
3. Recalculated c-constant using only data from specific arc (r^2 = correlation coefficient on linear regression).
4. Recalculated extrapolated flux using C-constant in previous column.
5. Where missing (or in parenthesis), values from column 4 are used in summation.

Table 8. Compilation of gas chemistries (median molar ratios) for 11 arc segments worldwide

Arc Segment	# Analyses	# Volcanic Centres	CO_2/S_t	CO_2/N_2	CO_2/N_2 (ex)	CO_2/He (x 10^5)	CO_2/Ar (x 10^3)	Refs.
Andes	70	5	5.7	61.1	73.2	2.92	10.7	[1-4]
Alaska-Aleutians	15	6	6.1	33.8	72.8	2.00	4.61	[5-7]
Lesser Antilles	44	2	5.0	64.6	-	1.26	n.a.	[8-10]
Central America	94	10	2.7	34.1	195.4	0.81	8.96	[11-18]
Indonesia (Sunda)	42	10	4.3	60.9	95.9	1.47	7.28	[19-25]
Italy	70	13	8.5	95.9	62.3	1.45	72.0	[12, 26-31]
Japan	83	9	6.5	18.9	24.1	0.76	4.39	[15, 32-46]
Kamchatka-Kuriles	37	16	1.7	14.1	23.8	0.95	2.82	[47-60]
New Zealand	214	84	28.7	53.0	102.3	1.05	4.03	[61-63]
Papua New Guinea/ SW Pacific	na	na	na	na	-	na	na	
Philippines	48	9	104.5	115.4	140.0	0.90	13.6	[12, 64-66]
GRAND TOTAL	721	165						

Footnote for Table 8

Gas compositional data sources

1 = Fischer et al. (1997); 2 = Lewicki et al. (2000); 3 = Sturchio et al. (1993); 4 = Giggenbach et al. (1986); 5= Symonds et al, (1990); 6 = Sheppard et al. (1992); 7 = Motyka et al. (1993); 8 = Chiodini et al. (1996); 9 = Hammouya et al. (1998); 10 = Brombach et al. (2000); 11 = Menyailov et al. (1986); 12 = Giggenbach (1992b); 13 = Taran, (1992); 14 = Rowe, et al. (1992); 15 = Goff and McMurtry (2000); 16 = Giggenbach and Corrales (1992); 17 = Janik et al. (1992); 18 = Taran et al. (1998); 19 = Allard, (1983); 20 = Giggenbach et al. (2001); 21 = LeGuern, (1982); 22 = Poorter, (1993); 23 = Fischer unpubl.; 24 = Delmelle et al. (2000); 25 = Sriwana et al. (2000); 26 = Chiodini, (1995); 27 = Cioni and D'Amore, (1984); 28 = Goff unpublished; 29 = Rogie et al. (2000); 30 = Minissale et al. (1997); 31 = Chiodini, (1994); 32 = Mizutani and Sugiura (1982); 33 = Symonds et al. (1994); 34 = Giggenbach et al. (1986); 35 = Nemoto et al. (1957); 36 = Mitzutani, (1962); 37 = Mitzutani and Sugiur, (1982); 38 = Symonds et al. (1996), 39 = Mitzutani, (1966); 40 = Giggenbach and Matsuo (1991); 41 = Mizutani et al. (1986); 42 = Matsuo et al. (1974); 43 = Shinohara et al. (1993); 44 = Ohba et al. (1994); 45 = Ohba et al. (2000); 46 = Kiyosu and Kurahashi (1984); 47 = Fischer et al. (1998); 48 = Taran et al. (1991); 49 = Menyailov and Nikintina (1980); 50 = Kirsanova et al. (1983); 51 = Taran et al. (1987); 52 = Taran (1985); 53 = Taran et al. (1995a); 54 = Taran et al. (1992); 55 = Menyailov et al. (1986c); 56 = Menyailov et al. (1986); 57 = Taran (1992); 58 = Taran et al. (1995b); 59 = Taran et al. (1995c); 60 = Taran and Korablev (1995); 61 = Giggenbach (1995); 62 = Christensen (2000); 63 = Giggenbach et al. (1993); 64 = Reyes et al. (1993); 65 = Delmelle et al. (1998); 66 = Giggenbach and Poreda (1993).

Table 9. Compilation of gas fluxes (mol/yr) for 11 arc segments worldwide

Arc Segment	SO_2[1] (x 10^9)	CO_2 (x 10^9)	N_{total} (x 10^8)	N_2 (ex)[2] (x 10^8)	He (x 10^4)	^{3}He[3]	Ar (x 10^6)
Andes	47.3	268.8	44.0	36.7	91.9	6.91	25.1
Alaska-Aleutians	0.56	3.43	1.01	0.47	1.71	0.13	0.74
Lesser Antilles	4.41	21.8	3.38	-	17.4	1.31	-
Central America	21.3	57.5	16.9	2.94	71.3	5.36	6.42
Indonesia (Sunda)	1.88	8.13	1.33	0.85	5.53	0.42	1.12
Italy	27.0	230.0	24.0	-	158.8	11.9	3.20
Japan	23.3	150.8	79.6	62.6	198.5	14.9	34.3
Kamchatka-Kuriles	1.67	2.77	1.97	1.16	2.90	0.22	0.98
New Zealand**	15.3	76.6	14.4	7.48	73.2	5.50	19.0
Papua New Guinea/ SW Pacific*	100.9	435.8	71.5	45.4	296.4	22.3	59.9
Philippines**	18.2	91.3	7.9	6.52	101.5	7.63	6.73
TOTAL (11 arcs)	261.8	1346.9	266.0	164.1	1019.1	76.6	157.5
TOTAL (Global)$^&$	315.7	1624.2	320.8	197.9	1228.9	92.4	189.9

1. From Table 7 (column 7)
2. Excess N_2 calculated using equation 3 (see text).
3. Calculated using average arc ^{3}He/^{4}He ratio = 5.37 R_A (Table 1)
* Flux calculations assumes Indonesia chemistry (from Table 8)
** Assumes CO_2/SO_2 molar ratio = 5
& Assumes additional 20.6% to all fluxes (see text)

Table 10. Volatile input at subduction zones.

Trench	Tonga	Kerm	Vanuatu	E.Sunda	Java	Sumatra	Andaman	Makran	Philip	Ryuku	Nankai	Marianas	Izu-Bon	Japan
Subd rate (mm/yr)	170	70	103	67	67	50	30	35	90	60	30	47.5	50	105
Trench Length (km)	1350	1400	1800	1000	2010	1000	1500	950	1550	1350	800	1400	1050	800
sediment subducted (g/y)	2.11E+13	2.74E+13	1.93E+14	5.74E+13	6.69E+13	1.36E+14	3.22E+14	2.86E+14	2.20E+13	1.81E+13	1.85E+13	5.89E+13	5.85E+13	4.82E+13
Ocenic crust subducted(g/yr)	4.64E+15	1.98E+15	3.75E+15	1.36E+15	2.72E+15	1.01E+15	9.10E+14	6.73E+14	2.82E+15	1.64E+15	4.86E+14	1.35E+15	1.06E+15	1.70E+15
FLUXES (Mmol/yr)														
H_2O sed	3.68E+04	5.70E+04	3.28E+05	1.77E+05	1.81E+05	4.13E+05	1.24E+06	6.69E+05	2.99E+04	4.17E+04	5.14E+04	1.71E+05	1.22E+05	1.64E+05
H_2O Crust	3.98E+04	5.18E+04	3.64E+05	1.08E+05	1.26E+05	2.58E+05	6.08E+05	5.39E+05	4.15E+04	3.43E+04	3.49E+04	1.11E+05	1.11E+05	9.10E+04
H_2O Available	1.41E+04	1.83E+04	1.29E+05	3.83E+04	4.46E+04	9.09E+04	2.15E+05	1.90E+05	1.47E+04	1.21E+04	1.23E+04	3.93E+04	3.90E+04	3.21E+04
CO_2 sed	0.00E+00	0.00E+00	1.06E+05	5.98E+04	9.68E+03	3.35E+03	3.01E+03	2.63E+05	1.61E+04	0.00E+00	0.00E+00	2.69E+04	3.85E+04	0.00E+00
CO_2org	4.79E+03	6.24E+03	4.38E+04	1.30E+04	1.52E+04	3.10E+04	7.32E+04	6.49E+04	4.99E+03	4.12E+03	4.20E+03	1.34E+04	1.33E+04	1.09E+04
CO_2 crust	2.26E+05	9.64E+04	1.82E+05	6.59E+04	1.33E+05	4.92E+04	4.43E+04	3.27E+04	1.37E+05	7.97E+04	2.36E+04	6.54E+04	5.17E+04	8.26E+04
N_2 sed	1.51E+02	1.96E+02	1.38E+03	4.10E+02	4.78E+02	9.74E+02	2.30E+03	2.04E+03	1.57E+02	1.30E+02	1.32E+02	4.21E+02	4.18E+02	3.44E+02
N_2crust	3.32E+03	1.42E+03	2.68E+03	9.68E+02	1.95E+03	7.23E+02	6.50E+02	4.80E+02	2.02E+03	1.17E+03	3.47E+02	9.61E+02	7.59E+02	1.21E+03
Hesed	9.28E-04	1.21E-03	8.48E-03	2.53E-03	2.94E-03	6.00E-03	1.42E-02	1.26E-02	9.67E-04	7.98E-04	8.13E-04	2.59E-03	2.58E-03	2.12E-03
Hecrust	2.04E-01	8.72E-02	1.65E-01	5.96E-02	1.20E-01	4.45E-02	4.01E-02	2.96E-02	1.24E-01	7.21E-02	2.14E-02	5.92E-02	4.67E-02	7.48E-02
^{36}Arsed	2.53E-05	3.29E-05	2.31E-04	6.89E-05	8.02E-05	1.64E-04	3.87E-04	3.43E-04	2.64E-05	2.18E-05	2.22E-05	7.07E-05	7.02E-05	5.78E-05
^{36}Arcrust	6.50E-04	2.78E-04	5.25E-04	1.90E-04	3.81E-04	1.42E-04	1.27E-04	9.42E-05	3.95E-04	2.29E-04	6.80E-05	1.88E-04	1.49E-04	2.38E-04

Table 10cont. Volatile input at subduction zones.

Trench	Kurile	Kamchat	Aleut	Alaska	Cascadia	Mexico	Centam	Colomb	Peru	SSand	N.Ant	S. Ant	TOTAL (mol/a)
Subd rate (mm/yr)	90	90	62	70	35	52	77	70	100	20	24	24	
Trench Length (km)	1650	550	1900	800	1300	1450	1450	1050	1500	800	400	400	
sediment subducted (g/y)	8.51E+13	2.95E+13	6.76E+13	7.87E+13	1.28E+14	1.75E+13	7.70E+13	3.25E+13	2.56E+13	4.77E+12	3.76E+12	3.16E+13	
Ocenic crust subducted(g/yr)	3.00E+15	1.00E+15	2.38E+15	1.13E+15	9.20E+14	1.53E+15	2.26E+15	1.49E+15	3.03E+15	3.24E+14	3.76E+12	1.94E+14	

FLUXES (Mmol/yr)

	Kurile	Kamchat	Aleut	Alaska	Cascadia	Mexico	Centam	Colomb	Peru	SSand	N.Ant	S. Ant	TOTAL (mol/a)
H_2O_{sed}	2.91E+05	1.19E+05	1.76E+05	1.86E+05	4.58E+05	3.99E+04	1.01E+05	7.31E+04	4.06E+04	9.44E+03	1.66E+04	1.14E+05	5.30E+12
H_2O_{Crust}	1.61E+05	5.57E+04	1.28E+05	1.49E+05	2.42E+05	3.31E+04	1.45E+05	6.14E+04	4.84E+04	9.01E+03	7.09E+03	5.97E+04	3.62E+12
$H_2O_{Available}$	5.68E+04	1.97E+04	4.51E+04	5.25E+04	8.55E+04	1.17E+04	5.13E+04	2.17E+04	1.71E+04	3.18E+03	2.50E+03	2.11E+04	1.28E+12
$CO_{2\ sed}$	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.38E+05	9.62E+04	4.41E+04	0.00E+00	3.18E+02	4.26E+02	9.06E+11
CO_{2org}	1.93E+04	6.71E+03	1.54E+04	1.79E+04	2.92E+04	3.98E+03	1.75E+04	7.39E+03	5.82E+03	1.08E+03	8.53E+02	7.18E+03	4.35E+11
$CO_{2\ crust}$	1.46E+05	4.87E+04	1.16E+05	5.51E+04	4.48E+04	7.42E+04	1.10E+05	7.23E+04	1.48E+05	1.57E+04	9.45E+03	9.45E+03	2.12E+12
$N_{2\ sed}$	6.08E+02	2.11E+02	4.83E+02	5.62E+02	9.17E+02	1.25E+02	5.50E+02	2.32E+02	1.83E+02	3.41E+01	2.68E+01	2.26E+02	1.37E+10
N_{2crust}	2.15E+03	7.15E+02	1.70E+03	8.09E+02	6.57E+02	1.09E+03	1.61E+03	1.06E+03	2.17E+03	2.31E+03	1.39E+02	1.39E+02	3.11E+10
He_{sed}	3.75E-03	1.30E-03	2.97E-03	3.46E-03	5.65E-03	7.70E-04	3.39E-03	1.43E-03	1.13E-03	2.10E-04	1.65E-04	1.39E-03	8.43E+04
He_{crust}	1.32E-01	4.41E-02	1.05E-01	4.98E-02	4.05E-02	6.71E-02	9.94E-02	6.54E-02	1.34E-01	1.42E-02	8.55E-03	8.55E-03	1.92E-06
$^{36}Ar_{sed}$	1.02E-04	3.54E-05	8.11E-05	9.44E-05	1.54E-04	2.10E-05	9.24E-05	3.90E-05	3.07E-05	5.72E-06	4.51E-06	3.79E-05	2.30E-03
$^{36}Ar_{crust}$	4.21E-04	1.40E-04	3.34E-04	1.59E-04	1.29E-04	2.14E-04	3.16E-04	2.08E-04	4.25E-04	4.53E-05	2.72E-05	2.72E-05	6.10E+03

<u>Footnote for Table 10</u>

Subduction Rate: from Plank and Langmuir (1998) and references therein.

Trench Length: from Plank and Langmuir (1998) and references therein.

Sediment subducted: calculated using subduction rate, trench length, sediment thickness and density for each arc (Plank and Langmuir, 1998).

Oceanic crust subducted: calculated using subduction rate, trench length (Plank and Langmuir, 1998) and assuming a thickness of the oceanic crust of 7 km and a density of 2.89 g/cm^3.

Fluxes: calculated using amount of sediments subducted or amount of oceanic crust subducted and concentrations of volatile species in the sediments or oceanic crust listed below.

H_2O sed: water in the sediments, excluding pore waters. Calculated using the amount of water stored in the sediments for each individual arc (Plank and Langmuir, 1998)

H_2O crust: amount of water stored in the oceanic crust - 3.4 wt% (Schmidt and Poli, 1998).

H_2O available: amount of water available (1.2 wt%) in the zone of arc magma generation (Schmidt and Poli, 1998)

CO_2 sed: amount of (carbonate) CO_2 in sediments of each individual arc (Plank and Langmuir, 1998)

CO_2 org: amount of reduced organic CO_2 stored in sediments. An average concentrations of 1 wt% is used (Bebout, 1995).

CO_2 crust: amount of CO_2 stored in the oceanic crust (carbonate CO_2). A value of 0.214 wt% is used (Alt and Teagle, 1999).

N_2 sed: amount of N_2 in oceanic sediments - 0.01 wt% (Bebout, 1995).

N_2 crust: amount of N_2 in oceanic crust - 0.001 wt% (Bebout, 1995).

He sed: amount of ^{4}He in oceanic sediments. An average value of 1.0 x10^{-6} cm^3 STP/g is used (Staudacher and Allegre, 1988).

He crust: amount of ^{4}He in oceanic crust. An average value of 1.0 x10^{-6} cm^3 STP/g is used (Staudacher and Allegre, 1988).

^{36}Ar sed: amount of ^{36}Ar in oceanic sediments. An average value of 2.7 x10^{-8} cm^3 STP/g is used (Staudacher and Allegre, 1988).

^{36}Ar crust: amount of ^{36}Ar in oceanic crust. An average value of 3.2 x10^{-9} cm^3 STP/g is used (Staudacher and Allegre, 1988).

Table 11: Carbonate (L), Sedimentary/organic (S) and MORB (M)
contributions (%) to arc CO_2 discharges*.

Arc Segment	L	S	M
Andes	0.56	0.33	0.09
Alaska-Aleutians	Nd	Nd	Nd
Lesser Antilles	0.71	0.17	0.03
Central America	0.59	0.31	0.06
Indonesia	0.74	0.13	0.12
Italy	Nd	Nd	Nd
Japan	0.67	0.13	0.18
Kamchatka-Kuriles	0.51	0.27	0.22
New Zealand	0.85	0.10	0.06
Papua New Guinea	Nd	Nd	Nd
Philippines	Nd	Nd	Nd

Nd = no data available (for Alaska-Aleautians, Italy, PNG and the Philippines).
* Endmember compositions for M, L and S used in the computations
are $\delta^{13}C$ (-6.5‰, 0‰, and -20‰) with corresponding $CO_2/^3He$ ratios
of 1.5×10^9; 1×10^{13}; 1×10^{13}.

Table 12. Ratio of output (via arc) to input (via trench) for major volatile species (CO_2, N_2 and H_2O) for selected arc segments.

Arc Segment	CO_2[1]			N_2 (excess)[2]	H_2O[3]	
	S OUT/ Org IN	L OUT/ Car[4] IN	L OUT/ (Car+ crst[5]) IN	OUT/ (Sed + crst) IN	OUT/ IN total[6]	OUT/ IN avl.[7]
Andes[8]	6.71	1.07	0.42	1.00	60.1	346.4
Alaska-Aleutians[9]	0.028	∞ [$]	0.010	0.013	0.27	1.76
Lesser Antilles[10]	0.46	20.8	0.79	-	5.52	46.2
Central America	1.02	0.14	0.097	0.14	11.7	56.0
Indonesia (Sunda)[11]	0.023	0.462	0.031	0.021	0.42	3.0
Italy						
Japan	1.80	∞	1.22	4.03	29.6	234.9
Kamchatka-Kuriles[12]	0.029	∞	0.0073	0.031	0.22	1.81
New Zealand[13]	1.29	∞	0.68	0.46	35.2	209.3
Papua New Guinea/ SW Pacific						
Philippines	2.38	4.20	0.44	0.30	63.9	310.5

1. CO_2 output resolve into L-, S-, and M-components (from Table 11).
2. N_2 excess = non-atmospheric N_2 (assumes all argon is air-saturated water derived – equation 3 in text).
3. H_2O output assumes arc H_2O/CO_2 ratio = 50 (Symonds et al., 1994).
4. Car = sedimentary carbonate input (CO_2 sed - from Table 10)
5. Crst = oceanic crust carbonate input (CO_2 crust – from Table 10).
6. Total water = sediment- and basement-hosted water only (excludes pore water).
7. Water available at zone of magma generation (1.2 wt.% - Schmidt and Poli, 1998).
8. Input from Columbia and Peru arcs (Table 10).
9. Includes input from Aleutians and Alaska arc (Table 10).
10. Includes input from both northern and southern Lesser Antilles (Table 10).
11. Includes input from Java and Sumatra (Table 10).
12. Includes input from Kuriles and Kamchatka arcs (Table 10).
13. Input taken for Kermadec arc (Table 10).
$ Infinity (zero carbonate input).

Table 13. Ratio of output (via arc) to input (via trench) for noble gas isotopes (^{3}He, ^{4}He, ^{36}Ar and ^{40}Ar) for selected arc segments.

Arc Segment[1]	^{3}He OUT/ IN	^{4}He OUT/ IN[2]	^{36}Ar OUT/ IN	^{40}Ar[3] OUT/ IN
Andes	488.8	4.55	88.9	103.3
Alaska-Aleutians	11.5	0.11	2.75	3.20
Lesser Antilles	1002	9.32		
Central America	744.9	6.94	39.1	45.5
Indonesia (Sunda)	34.6	0.32	3.63	4.22
Italy				
Japan	2767	25.8	288.5	335.3
Kamchatka-Kuriles	17.4	0.16	3.49	4.06
New Zealand	888.8	8.28	152.0	176.7
Papua New Guinea/ SW Pacific				
Philippines	879	8.19	39.7	46.2

1. See Table 12 for arcs used in input computation.
2. Input ^{3}He/^{4}He ratio = 0.05 R_A (radiogenic helium)
3. Output ^{40}Ar/^{36}Ar ratio = 401 (Table 4); input ^{40}Ar/^{36}Ar ratio = 345 (average of sediment and oceanic crust – from Staudacher and Allegre, 1988).

Table 14. Average global volatile fluxes out of volcanic arcs (F_{arc}) and mid-ocean ridges (F_{MORB}), and into subduction zone (F_{sub}) together with total surface inventories (atmosphere+oceans+crust).

Volatile	**F_{arc} mol/yr**	**F_{sub} mol/yr**	**F_{arc}/F_{sub}**	**Surface Invent. (mol)**	**F_{MORB} mol/yr**	**Surface/F_{MORB} yr**
H_2O	8.12E+13	8.92E+12	9.10	5.80E+23	2.90E+13	2.0E+10
SO_2	3.16E+11	(4.11E+12)	0.077	5.33E+20	(2.67E+12)	2.0E+08
CO_2 (L+S)	1.45E+12	3.46E+12	0.42	7.00E+21	2.20E+12	3.2E+09
N_2 (S + Crst)	1.98E+10	4.48E+10	0.44	2.74E+20	1.00E+09	1.8E+11
^{3}He	9.24E+01	1.40E-01	660	9.14E+13	1.00E+03	9.1E+10
^{4}He	1.23E+07	2.00E+06	6.2	3.61E+18	8.93E+07	4.0E+10
^{40}Ar	1.90E+08	2.90E+06	65.5	1.64E+18	4.00E+07	4.1E+10
^{36}Ar	4.74E+05	8.40E+03	56.4	5.55E+15	1.00E+03	5.55E+12

Footnote to Table 14

F_{arc}: total global flux of volatile species from subduction zones - calculated by summing individual arc volatile fluxes and adding additional 20.6% (see Table 9). The water flux was calculated using the CO_2 flux (Table 9) and assuming a H_2O/CO_2 ratio of 50. The CO_2 (L + S) – limestone- + sediment-derived CO_2 is the total arc CO_2 flux (Table 9) multiplied by 0.89 (the average L+S value for 7 arcs worldwide – Table 11). ^{36}Ar flux is calculated using the total Ar flux (Table 9) and an average ^{40}Ar/^{36}Ar ratio of 401 (Table 4).

F_{sub}: total global subduction of volatile species. Calculated by summing flux values of individual arcs (Table 10).

Surface Invent.: global inventory of volatile species currently at the Earth's surface.

   H_2O: from Marty and Dauphas (2002.)

   SO_2: surface/F_{MORB} from Marty and Dauphas (2002)

   CO_2: from Zhang and Zindler (1993)

   N_2: from Pepin (1991)

   ^{3}He: from Ozima and Podosek (1983) – assumes ^{20}Ne inventory of atmosphere and planetary ^{3}He/^{20}Ne ratio of 0.0315. Present atmosphere abundance is lower because of escape to space.

   ^{4}He: from Ozima and Podosek (1983) – radiogenic ^{4}He released into atmosphere taken as 2.2 times atmosphere ^{40}Ar abundance. Present abundance is much lower because of escape to space.

   ^{36}Ar &^{40}Ar: from Ozima and Podosek (1983)

F_{MORB}: flux of volatiles from the mantle, approximated by MORB flux.

   H_2O: from Marty and Dauphas (2002)

   CO_2 :from Marty and Tolstikhin (1998)

   N_2: using ^{3}He flux (1000 mol/yr) from Craig et al. (1975) and MORB $N_2/^3$He ratio of 1 x 10^6 (Sano et al., 2001).

   ^{3}He: from Craig et al. (1975)

   ^{36}Ar: calculated from the MORB ^{3}He flux and MORB ^{36}Ar/^{3}He ratio = 1 (Tolstikhin and Marty 1998).

Figure Captions

Figure 1. Locations map of arc and back-arc systems for which helium isotope data are available (Tables 1 and 4 Note Italy is omitted). Trenches are marked by barbed lines (filled barbs = accrectionary trenches; open barbs = no accretionary prism). Figure modified from Von Huene and Scholl (1991).

Figure 2. Neon isotope systematics of arc-related volcanism. Arc data from Table 2, MORB-trend from Sarda et al. (1988) and crustal-neon trend from Kennedy et al. (1990). mfl = mass fractionation line.

Figure 3. Neon isotope systematics of back-arc volcanism. Back-arc data from: Honda et al., 1993b (Lau Basin); Ikeda et al., 1998 and Sano et al., 1998a (Mariana Trough); and Shaw et al., 2001 (Manus Basin). Loihi-Kilauea (L-K) trend from Honda et al. (1991), Manus trend from Shaw et al. (2001). mfl = mass fractionation line.

Figure 4. Log-log plot of cumulative frequency of number of Central American volcanoes (N) having SO_2 flux equal or greater than f (following methodology of Brantley and Koepenick, 1995). Data from Andres and Kasgnoc (1998).

Figure 5. Ternary plot of CO_2 provenance in arc-related volcanism (data from Table 11). L, S, and M represent limestone, sediment and mantle wedge respectively.

Figure 6. Volatile flux ratio (F_{arc}/F_{sub}) versus mean degassing duration (MDD) for 4 major (S, C, H_2O, N_2) and 2 noble gas (He, Ar) volatile species following approach of Marty and Dauphas (2002).

Map showing circum-Pacific subduction zones and trenches. Labels (clockwise): 90°, 145°, 160°, 105°, 50°, 30°, Kamchatka, Alaska, Cascades, Ryuku, Kuril Is., Aleutian, Japan, Nankai, Izu-Bonin, Lesser Antilles, Mariana Trough, Marianas, Mexico, Central America, Colombia, Equator 0°, Phil., Manus Basin, Tabar, Lau Basin, Sumatra, Banda, New Hebrides, Tonga, Peru, Java, N Fiji Basin, Kermadec, North Chile, New Zealand, Central Chile, 30°, 60°

Central America Volcanoes

Linear regression
gradient = -0.46
r^2 = 0.72

$\log(f_{SO_2})$ (Mmol/yr)

Log (N)